VTT Technical Research Centre of Finland

Sustainable Binders from Bark (SusBinders)

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Executive summary

The overall aim of the project was to systematically evaluate ***the suitability of softwood tannins for wood resin and hot melt applications including the development of adhesive formulations*** for both applications. Furthermore the aim is to ***improve the process economy***. Therefore, optimizing the extraction step and improving the extraction yield of tannins and the stability of tannins in liquids were project objectives.

In the project, VTT Technical Research Centre of Finland Ltd. (coordinator), the Natural Resources Institute Finland (Luke) and the South-Eastern Finland University of Applied Sciences (Xamk) have evaluated technologies for an industrial production method of tannin from softwood bark and performed application tests.

The project delivered a ***realistic estimate of the yield for crude tannin in an industrial set-up***. The yield of solubilized material in pilot extractions were up to 14 w% from finely ground spruce bark in a batch process in VTT's pilot extraction, 10 w% in a batch process with flow through in Luke's pilot extraction and up to 7 w% in the newly developed continuous extraction using 8% consistency at Xamk. The lower yield compared to up to 20% in the literature, can be partly explained by the fact that bark stream in pulp and saw mills contain substantial amounts of wood. In project samples from a saw mill, 20 % and 30% wood content were estimated for bark from spruce and bine bark, respectively. The yield of crude tannin from pine bark remained lower in pilot extraction trials with 7.8 w% yield. In agreement with earlier findings, the most potential crude tannin extracts from spruce bark contained ~45% phenolic compounds, ~40% carbohydrates and ~5% ash for batch extractions at 90 or 110 °C.

An approach to produce a ***purified tannin product enriched in phenolic compounds*** was developed. The performed steps were liberation of monosaccharides from the crude tannin by enzymatic hydrolysis of carbohydrates followed by nanofiltration in order to remove the liberated monosaccharides. In total, 50% of carbohydrates were liberated with an enzyme dosage of 10 mg/g DM. The fractionation with a nanofiltration membrane enabled 9-fold concentration of the enzymatically treated crude spruce bark tannin in pilot scale with successful removal of the liberated carbohydrates, resulting in enriched phenolic fraction. However, also the permeate contained some phenols. Thus, both monosaccharides and low molecular weight phenols can pass through NFG membrane, enlarging the average molecular weight of the fraction.

In a ***shelf life study***, it was observed that aqueous crude tannin products can be stored at +4°C for a period of 7 months preserving the reactivity against formaldehyde and without notable microbiological growth.

The tannins from softwood bark were tested as ***phenol replacement in phenol-formaldehyde resins*** (thermosets) for plywood gluing and at a replacement level of 30%, crude pine tannin, the resins showed comparable adhesive bond strength as commercial wood resins in laboratory testing. Even 50% replacement level gave reasonable bond strength. Future work should be directed towards formulation to ensure water resistance. It could be demonstrated that a mixture of tannin and poly(DL-lactide-co-ε-caprolactone) is a potential ***hot melt adhesive***. The copolymer can be used as a hot melt adhesive by itself, but the processability and adhesion towards uncoated boxboard increased with tannins.

1. Background and introduction

The Finnish wood working industry produces roughly 6.5 M m^3 conifer bark in sawmills, plywood and veneer production and from mechanical and chemical pulp mills. Currently, this side-stream is combusted for energy at industrial, and to a lesser extent, at municipal heat and power plants (Alakangas, 2000). Bark contains many valuable components, which could be extracted and upgraded to increase profitability of the wood working industry, create new businesses and jobs in Finland and promote bioeconomy. Moreover, there is a market need for chemicals from renewables since chemical companies are actively looking for new sustainable, green, non-toxic starting materials and chemicals.

Besides carbohydrates and lignin, softwood bark from Nordic wood species contains extractives like tannins (ca. 10% of dry matter). Tannins of other wood species are industrially produced and utilized. The global production of tannin is currently ca. 0.1 Mt/a mainly from wood species such as Mimosa/Wattle (Acacia), Quebracho (Schinopsis), oak and chestnut. The major application areas is traditional leather tanning. Other niche markets exist for bark extractives e.g. in viticulture and in the pharmaceutical sector. Alternative applications have been studied, e.g. for tannin from Radiata pine bark, adhesive applications. Commercial-scale wood composite production using tannin-based adhesives has been operational a few decades ago in Australia, New Zealand and Chile (Li and Maplesden, 1998).

Nordic softwood bark is a promising raw material for tannin extraction. It is available all year round and it is collected at the pulp and sawmill sites. After extraction, the bark residue can be returned back to the process for burning and removal of the tannins from bark does not reduce its burning value. The debarking units at saw mill and pulp mill yards vary greatly in size in Finland. On average, a large pulp mill like UPM Kaukas, Stora Enso Imatra or Metsä Fibre Joutseno uses annually 3-5 Mm3 wood producing 110 000 – 170 000 t bark per year (assuming similar amount of bark in all tree species). On the other hand a large Finnish saw mill like Metsä Wood Lappenranta sawmill, or UPM Savonlinna plywood mill uses 500 000 m3/a wood producing 20 000 – 30 000 t/a bark. Debarking at pulp mills creates also effluents such as bark press water that is naturally rich in bark-derived polyphenolics. Utilisation of these effluents for collecting valuable polyphenolic compounds is also of great interest.

There are challenges for the commercialization of softwood tannins connected to estimates for high processing cost and problems related to extraction yields and quality of the extracted tannin (impurities) Therefore, utilization of Nordic softwood tannins has been largely neglected. However, condensed tannins could be produced in more than 10% yield from softwood bark and they have potential in several large volume applications. The most promising applications for tannins are seen in resins and wood adhesives. In addition, tannins have been studied for foam applications and as flame retardants and they have been shown to have antimicrobial and nutraceutical properties.

Based on this background, the following objectives were set for the SusBinders project.

The overall aim of the project was to **systematically evaluate the suitability of softwood tannins for hot melt and wood resin applications** and **to develop adhesive formulations** for both applications. Furthermore the aim is to improve the process economy. This will be done by optimizing the extraction step and improving the extraction yield of tannins and the stability of tannins in liquids.

More specifically the project goals are:

- Improve the extraction yield by 50%, aiming at 75% extraction yield from the theoretical
  - by optimizing the batch extraction process
  - by developing a continuous extraction process
- Evaluate the applicability of crude tannin in resin and adhesive applications
- Develop a partial tannin purification procedure
- Develop a minimum threshold values for tannin purity and quality to be used in wood-resins and hot-melt glues
- Develop a 100% phenol-free wood-resin and replace formaldehyde with a non-toxic cross-linker
- Improve stability of tannins in liquids to allow use of tannins without drying
  - Retaining 80% of formaldehyde reactivity within 6-months
- Determine optimal reactor design and processing machines for the extraction process
- Demonstrate the whole concept for tannin production
  - Pilot scale extraction using Luke's 300 liters reactor located in Bioruukki
  - Ultrafiltration: purification and concentration
  - Spray-drying if needed
- Make plans for integration of extraction plant to a mill to reduce costs
- Techno-economic feasibility and scenario analyses developed for the production concepts
- Market and patent survey
- Disseminate project results (patent and/or publish)

The project was organized in seven work packages as illustrated in Figure 1.

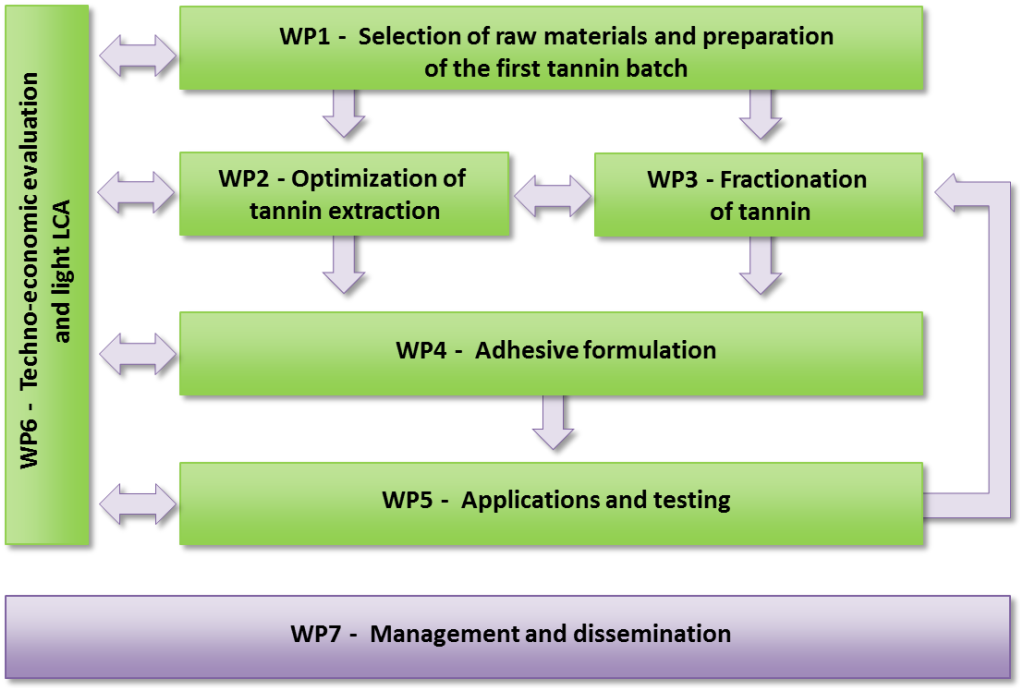


Figure 1. Work Packages (WP) of the project and their interplay.

2. WP1. Selection of the raw materials and preparation of the first tannin batch

Task 1.1 Selection of raw materials (All partners)

The aim was to acquire fresh wet bark originating from Nordic spruce and pine trees from e.g. a pulp mill. In the first steering group meeting, this was confirmed. A Finnish pulp mill supplied the project with several bark batches (Table 1). Storage of large amounts of fresh, ground bark at refrigerate temperatures (4°C) was challenging and therefore, the batches from **summer 2018 (long hot period) was not optimal** for the project work. The last batch was obtained, ground and pilot extraction performed within a five week period (December 10th 2018 - January 17th 2019). Continuous extraction trials continued from this batch until May 2019.

Table 1. Information on bark samples used in the SusBinders project. The bark batches highlighted with green suffered from microbial activity during storage. MF = Mechanical fraction from debarking, S/P=Spruce/Pine, M/S = milling type 1/milling type 2

Code	Bark type	Sampling date	Size	Supplier	Processing	Utilization
MF-S-M **MF-S-S**	saw mill spruce bark	14.8.2017	500 kg	Saw mill	Ground in an industrial setting	WP1: Pilot extraction at VTT WP2. Optimization of tannin extraction Luke and Xamk Crude tannin extract used in WP3 and WP4
MF-P-M **MF-P-S**	saw mill pine bark	14.8.2017	500 kg	Saw mill	Ground in an industrial setting	WP1: Pilot extraction at VTT WP2. Optimization of tannin extraction Luke and Xamk Crude tannin extract used in WP3 and WP4
MF-S2-M	pulp mill spruce bark	May-June 2018		Pulp mill	Ground in an industrial setting	WP2. Optimization of tannin extraction Luke and Xamk Crude tannin extract used in WP3
MF-P2-M	pulp mill pine bark	May-June 2018		Pulp mill	Ground in an industrial setting	WP2. Optimization of tannin extraction Luke and Xamk Crude tannin extract used in WP3
MF-S3-M	pulp mill spruce bark	December 2018.	1000 kg, 4 large bags	Saw mill	Ground in an industrial setting	WP2. Tannin extraction in pilot scale Luke and Xamk Extract used for piloting in WP3

Task 1.2 Preparation of crude tannin batch (VTT)

The target was to supply the project with crude tannin (min 10 kg) using batch reactor extraction at VTT.

The production of crude tannin is described in detail in the deliverable report 'D1.2 Pilot production of crude tannin in 10 kg scale'. Pine and spruce bark from saw mill were delivered to and industrial facility for size reduction. The samples were coded as shown in Table 1:

- MF-P1-S for pine bark ground in an industrial setting 1,
- MF-P1-M for pine bark ground in an industrial setting 2 and
- MF-S1-S and MF-S1-M correspondingly for ground spruce bark.

The extraction parameters, 90°C, 2 h, were chosen based on a literature survey (D1.1. Literature and market study, see Table 1) and on earlier experience. Tannin was extracted in 47.5 … 77.9 kg scale (dry bark content) at 90 °C for 2 h from pine and spruce bark, respectively. The yields are shown in Table 2 and composition in Figure 2.

Table 2. Information on pilot extraction trials at VTT for production of crude tannin in autumn 2017.

	Extraction of spruce bark		**Extraction of pine bark**	
Bark code	**Industrially ground spruce P16S** **MF-S-S**	**Industrially ground spruce fine** **MF-S-M**	**Industrially ground pine P45 + P16S** **MF-P-S**	**Industrially ground pine fine** **MF-P-M**
Dry bark to extraction, kg	47.5	75.0	76.9	77.9
Dry solids in extraction, %	5.5	5.5	6.6	5.5
pH	4.65	4.62	4.52	5.09
Theoretical tannin yield* (dry), kg	4.96	10.3	3.47	6.06
Theoretical tannin yield (dry solids) based on dry bark, %	**10.4**	**13.7**	**4.5**	**7.8**
Tannin code	tannin powder MF-S-S-T	tannin powder MF-S-M-T	tannin powder MF-P-S-T	tannin powder MF-P-M-T
Isolated tannin yield, kg	**3.4**	**8.2**	**2.2**	**4.0**
Dry solids, %	93.3	95.9	95.3	95.1
Tannin yield (dry solids) based on dry bark, %	**6.7**	**10.9**	**2.7**	**4.9**

*Solubilized yield (kg) = Dry solids in solute after filtration multiplied by whole mass of water in the system consisting of added water and the moisture contained in the bark. Solubilized yield (%) = mass of the extracted compound divided by the mass of the original dry bark.

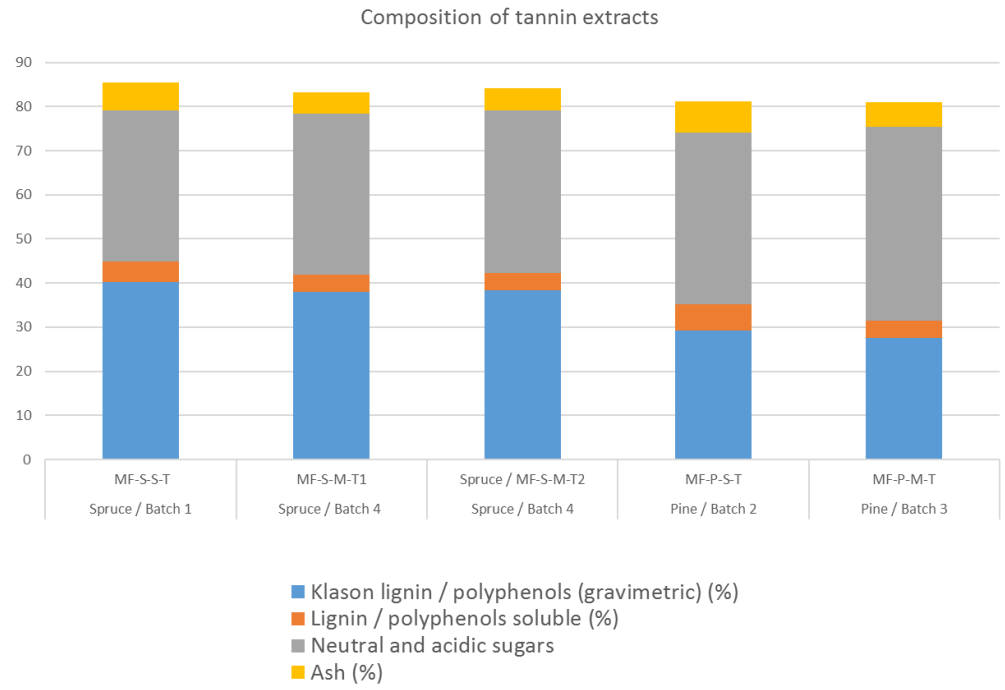


Figure 2. Composition of the extracted crude tannins from the pilot extraction at VTT in autumn 2017.

The major conclusions of the extraction trials were:

- The yields of the extracted crude tannin were lower than expected, maximum of 13.7% solubilized spruce crude tannin and 7.8% pine crude tannin. These relatively low yield of crude tannins are partly explained by high amount of wood in the bark (20% in spruce bark and 30% in pine bark).
- There was severe challenges in processing of coarse bark with the equipment available at VTT chemistry pilot. Thus, alternative filtration was used during the extractions.
- Processing of finely ground bark went smoothly.
- In both cases, processing took minimum one week from extraction of bark to dry (spray dried) tannin powder. This may have negative effect on tannin quality, since it is known that tannin autocondensation and rearrangement reactions can take place in aqueous solutions.
- Effects on water solubility when dissolving the dried crude tannins to water may be indication of possible condensation. However, tannin extracts were almost fully soluble to 0.1M NaOH solution. This is an encouraging result, since phenol-resins for wood adhesives are synthetized in alkaline water solutions.
- The crude tannin contained 35-45 % phenolic compounds, 35-45% carbohydrates and approximately 5% of inorganic compounds (ash).
- The results indicate that a realistic yield for crude tannins from industrial bark would be around 14%. Some improvement might be possible taking into account that a continuous line would operate at the mill omitting breaks due to sample transport.

Dry crude tannin was used in development of adhesive formulations (WP4). Part of the extract was concentrated and used in for developing the purification of crude tannin in WP3.

Task 1.3 Literature and market study (VTT, Luke, Xamk)

The aim of the literature and patent survey was to update the knowledge on public information related to softwood tannin extraction and their use in adhesive applications. In a joint effort, VTT, Luke and Xamk reviewed literature (D1.1. Literature and market study).

The major conclusions were:

Unsatisfactory extraction yields, low purity (carbohydrate contaminants) and high viscosity are common challenges related to the use of Radiata pine bark extracts for adhesive applications. Considerably less information is available on the use of Nordic softwood species in tannin extraction.

Typically, tannins are extracted with hot water and higher temperature increases the yield. However, with very high temperature, more carbohydrates are extracted and quality of tannin extract decreases. In some cases extraction chemicals such as sodium bisulphite and urea are used to increase the yield and also to obtain better quality tannin.

Currently, the majority of tannins are produced from tropical wood species such as Mimosa/Wattle (Acacia) and Quebracho (Schinopsis) in South-Africa and South-America. Tannin yields and purities are good from these tropical trees. Tannin yields and polyphenol content from Norway spruce bark (yield ~10%, polyphenols ~50%) and Scots pine bark (yield ~10%, polyphenols <50%) are rather low. This makes utilization of Nordic softwood bark in tannin production challenging. However, bark is available all year round from several mills in Finland and there could be benefit in integration of extraction plant to a mill.

Polyphenol content in tannin extracts can be increased by using enzymes to hydrolyze oligo- or polymeric carbohydrates to monosaccharides. Small monosaccharides can be then filtrated off by using nano- or ultrafiltration. Enzymes such as glucosidases, hemicellulases and pectinases have been used successfully to hydrolyze at least part of the carbohydrates. Moreover, membrane filtration techniques have been applied to enrich polyphenol content in tannin extracts. However, there are still some challenges such as insufficient enzyme activity, or fouling problems in filtration.

Leather tanning is the most important application of condensed tannin with ~65% market share, followed by tannin wood adhesives (~20%). There are several companies who use tannins to manufacture exterior grade weather resistant panels, but these are based on Mimosa/Wattle or Quebracho tannins. There are only handful of publications about utilization of Norway spruce or Scots pine tannins in PF resins. Pine tannin (60%) and spruce tannin (80%) was used in plywood resins. However, only 20% of tannin extract could be used without reducing wet bonding strength. Moreover, mechanical properties of particleboards bonded with unmodified extracts were low, if no isocyanate was used as additional fortifier. In another publication, spruce tannin was used to partially replace Quebracho tannin in MDF up to 60% with boards still meeting specifications of moisture resistance. Moreover, boards with 100% spruce tannin-adhesive met specifications for indoor use.

In hot melt adhesives, tackifier resins are typically rosin esters, hydrocarbon resins, terpene resins and hydrogenated hydrocarbon resins. Reports on testing of tannins in hot melt adhesives are very limited. In one patent, phenolic tannic acid was suggested to improve the adhesive strength and the wetting of substrate.

There used to be three tannin extraction plants in Sweden using spruce bark as raw material until 1950's (AB Tannin, Garvämnes AB Weibull and AB Svenska Garvämnesfrabriken), but to our knowledge, there is no significant production of tannins from Nordic softwoods currently. However, there is one small tannery (Böle Tannery) in Sweden, who uses spruce tannin in leather tannin-process. http://www.boletannery.com/.

Milestones and deliverables

- **MS 1.1** Raw materials selected (Month 1)
- **MS 1.2** Selection of extraction conditions for large crude tannin batch (Month 1)
- **MS 1.3** Crude tannin min. 10 kg prepared (Month 3)
- **MS 1.4** Literature and market study completed (Month 3)

- **D 1.1** Literature and market study (Month 3) 30.11.2017
- **D 1.2** Crude tannin min. 10 kg (Month 3) 15.11.2017

3. WP2. Optimization of tannin extraction

Task 2.1 Bark pre-treatment and shredding (Luke)

The treatment of the bark samples before extractions is described in Chapter 2. 'WP1. Selection of the raw materials and preparation of the first tannin batch'.

Spruce and pine bark samples from sawmill was grinded in an industrial setting (Task 1.1). Additional pine bark samples from pulp mill were milled using Fritsch Pulverisette crushing and cutting blade mill with a 6 mm sieve.

Task 2.2 Optimization of the tannin extraction in batch process (Luke)

For optimization trials, grinded bark samples were extracted with hot water using Thermo Scientific™ Dionex™ ASE™ 350 extraction system. ASE 350 system allows unattended extraction of up to 24 samples under precise temperature. Extraction takes place under pressure (103 bar). Extractions were performed in three different temperatures 60, 75 and 90 °C and additional samples with 110 and 140 °C with 10 g of ground bark in 100 ml extraction cell. Extraction time was 120 minutes.

Spruce and pine bark samples were extracted with hot water and additional chemicals. The aim of the chemical addition was to increase tannin yield. Sodium bisulfite 20 g/l ($NaHSO_3$), urea 20 g/l ($CO(NH_2)_2$), sodium benzoate 10 g/l ($NaC_7H_5O_2$) and sodium carbonate 5 g/l (Na_2CO_3) additions were used in the same extraction conditions.

Samples were analyzed with UV-spectrometer to obtain tannin yield. Stiasny number was used to measure dried extract reactivity to form formaldehyde resin. Total dissolved solids (TDS) and pH of the samples were measured in extracts. Extracts were further lyophilized into dryness and stored at -18 °C for UV-, Stiasny number and tannin analysis with HPLC.

Condensed tannin (CT, proanthocyanidins) was determined by HPLC after thiolytic degradation. Samples were weighed (20–40 mg) into 1.5 ml Eppendorf vials and 1 ml of depolymerization reagent (3 g cysteamine/4 ml 13M HCl/56 ml methanol) was added. The vials were sealed and incubated for 60 min at 65°C, after which the reaction was stopped using an ice bath. Samples were filtrated into HPLC vials and analysed by Agilent 1100 HPLC device equipped with an Inertsil ODS-3 column (150 × 4 mm i.d., 3 µm; GL Sciences Inc., Torrance, CA). The mobile phase consisted of (A) 50 mM phosphoric acid, pH 2.5 and (B) acetonitrile. Elution was started with 5 per cent acetonitrile, isocratically for 5 min, followed by a linear gradient to 20 per cent in 30 min, to 50 per cent in 10 min, isocratically for 5 min, and back to the starting point in 2 min. The post-time was 6 min before the next injection. The flow rate was 0.7 ml/min and injection volume 10 µl. Elution was monitored by diode array detection (DAD; λ1 = 270 nm, λ2 = 280 nm) and fluorescence detection (FLD; λex = 280 nm, λem = 324 nm). CT degradation products, i.e. free flavan-3-ols (terminal units) and their cysteaminyl derivatives (extension units), were quantified using external standards of catechin, epicatechin, gallocatechin, epigallocatechin, and thiolyzed procyanidin B2. Cysteamine, catechin, epicatechin, gallocatechin, and epigallocatechin were purchased from Sigma-Aldrich Finland Oy (Espoo, Finland). Procyanidin B2 was obtained from Extrasynthese (Lyon, France).

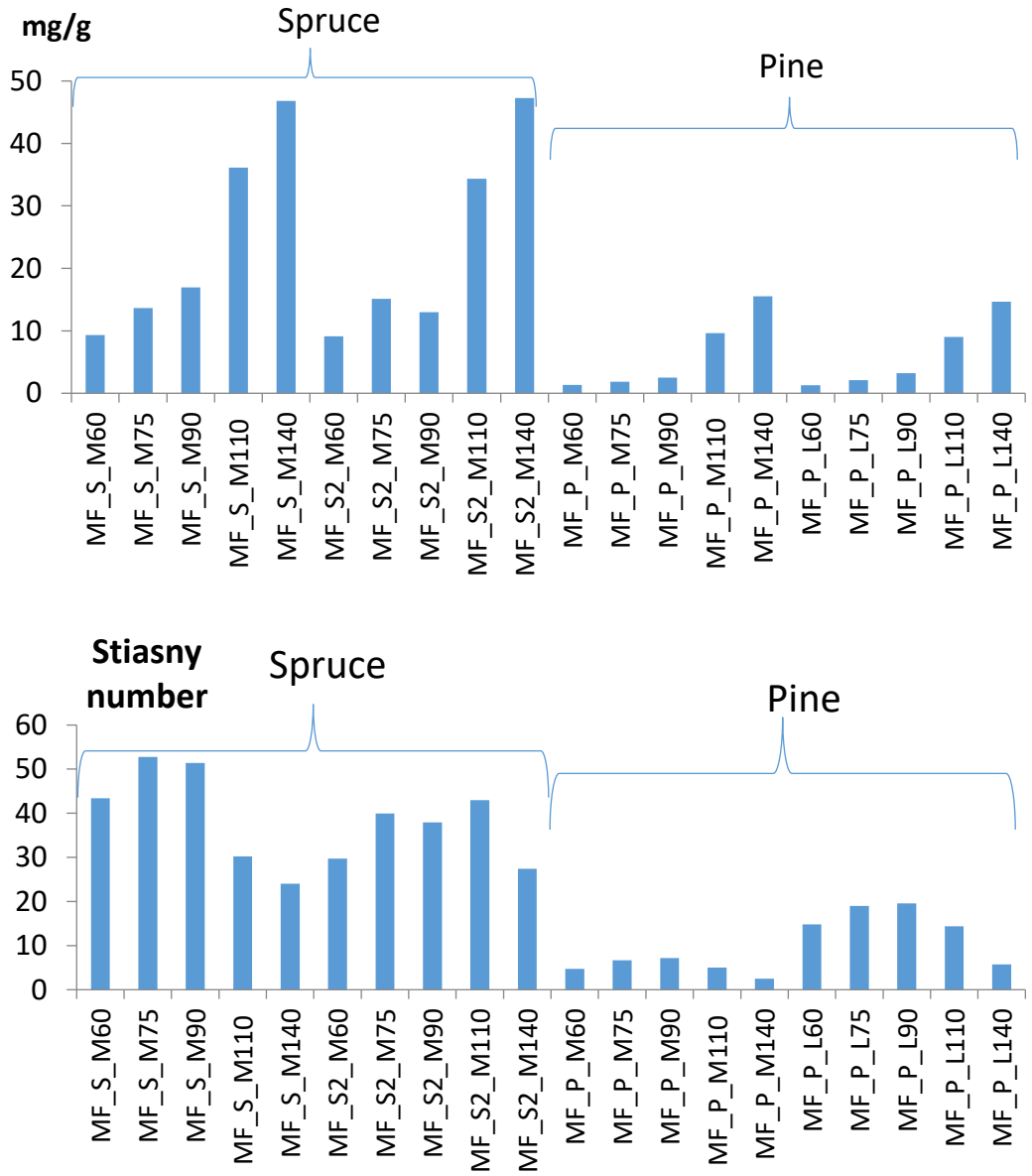
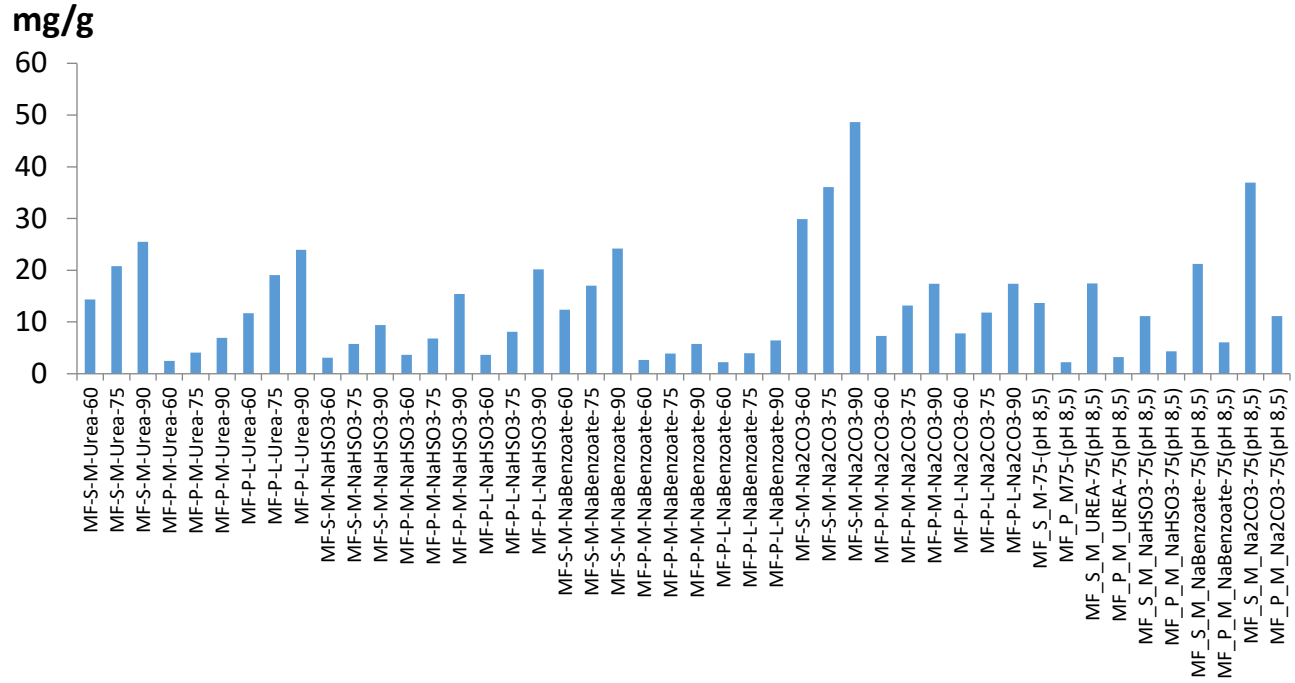


Figure 3 The amount of tannins/polyphenols analysed by UV-method and Stiasny no of the water extracts at different temperatures. Abbreviations: MF=Mechanical fraction from debarking, S = spruce, P = pine, M =milled in industrial facility, L = milled with crushing and blade mill at Luke, extraction temperatures (60, 75, 90, 110 and 140 temperatures). Pine shows much less tannins in the extract and in spruce, and the amount analysed by UV-method seems to increase with increasing temperature. However, Stiasny no decreases after 90 degrees indicating that extract may contain other phenolic or carbohydrate compounds than tannins.



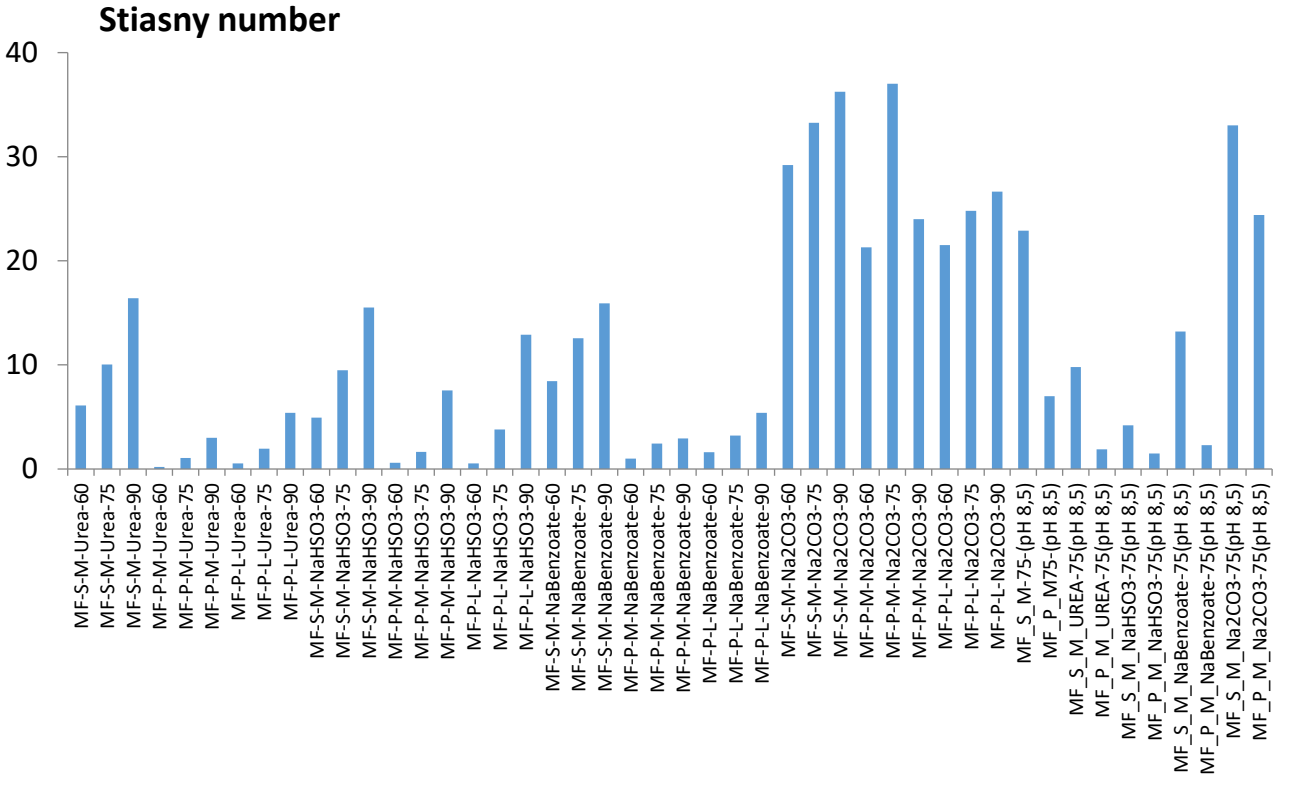


Figure 4 The amount of tannins/polyphenols measured by UV-method and Stiasny number of hot water extracts after chemical additions. Legend on x-axis shows wood species (S = spruce, P = pine), pretreatment (M = milled in industrial facility, L = milled with crushing and blade mill at Luke), extraction temperatures (60, 75 and 90 °C) and chemicals that were added (sodium bisulfite 20 g/l ($NaHSO_3$), urea 20 g/l ($CO(NH_2)_2$), sodium bentzoate 10 g/l and sodium carbonate 5 g/l (Na_2CO_3)).

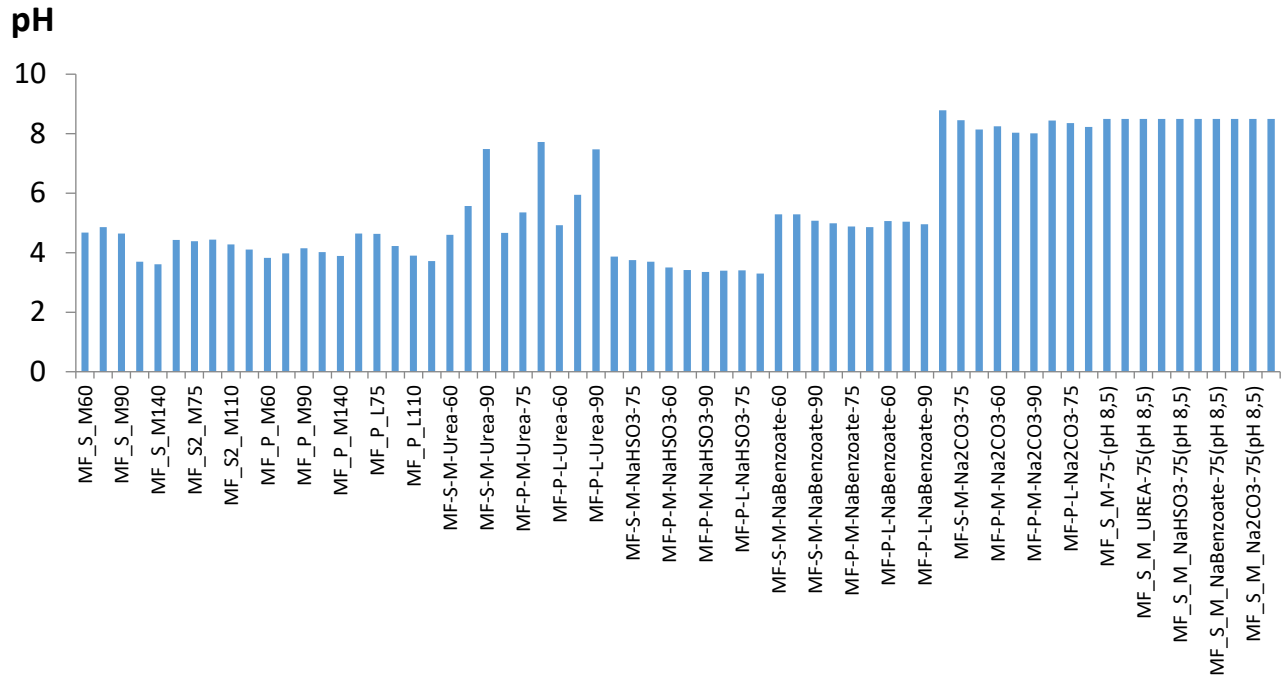


Figure 5 pH of the different extractions. For abbreviations, see Figure 4

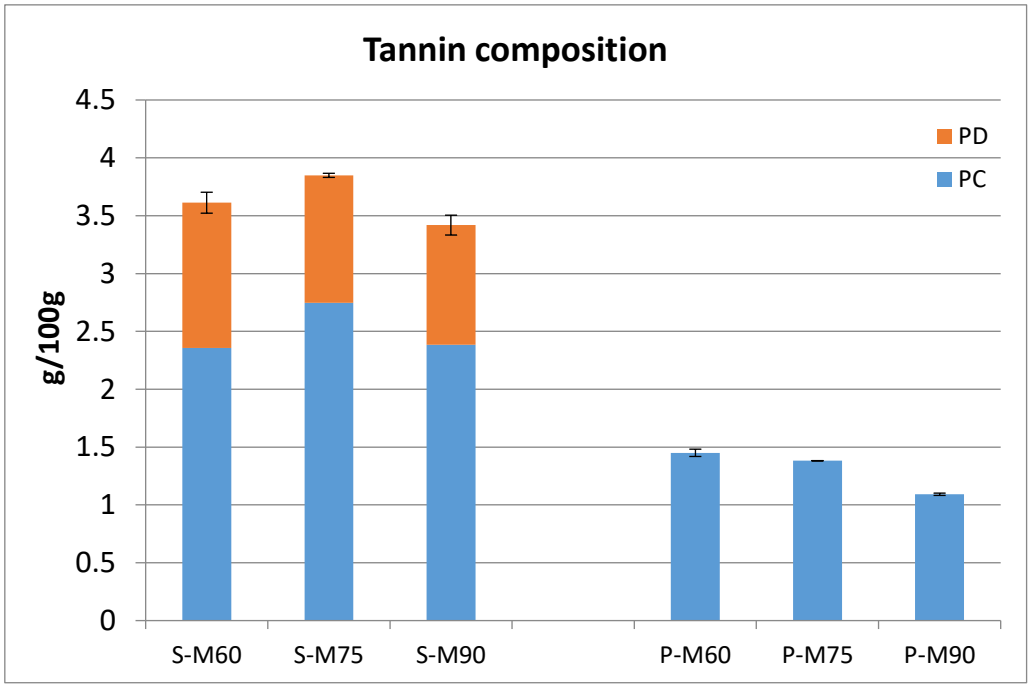


Figure 6 Tannin composition was further analysed with HPLC-UV thiolysis method by Jarkko Hellström at Luke. S = spruce, P=pine and different extraction temperatures 60, 75 and 90 degrees). PC = procyanids , PD = prodelfdinidins. Note, the amount is g per 100 g of extract

Table 3 Tannin composition of different hot water extracts expressed as mg/g bark (dry weight)

Sample	DP	PC	PD	mg/g
MF_S_M60	3.9	64.3	35.7	0.9
MF_S_M75	3.7	71.7	28.4	1.2
MF_S_M90	3.8	71.7	29.7	1.2
MF_P_M60	1.9	100.0	0.0	0.4
MF_P_M75	1.9	100.0	0.0	0.4
MF_P_M90	1.9	100.0	0.0	0.5

S = spruce, P = pine, different extraction temperatures (60, 75 and 90 degrees), DP = degree of polymerization, PC = procyanids , PD = prodelfdinidins, yield on the basis of dry weight of bark.

According to the HPLC analysis (Figure 6 and Table 3), it seems that condensed tannins are extracted only in a small amount compared to the total amount of extract. Extracted molecules have a low degree of polymerization, on the average 2 - 4 units in each.

In conclusion, higher extraction temperature increased tannin yield in all extractions (Figure 3 and Figure 4). Tannin yield was also higher when spruce bark was extracted. Urea and sodium bisulfite additions increased significantly the yield from pine bark. In case of pulp mill pine bark the yield of pine was higher than spruce bark. When analyzing UV-measurements and Stiasny no. together, addition of sodium carbonate or extraction at 110 degrees seem to result the highest yield. If both pine and spruce are compared, the addition of sodium carbonate resulted in the best yields.

The pH value of the extracts was usually in the range of 4-5. Sodium carbonate addition increased extracts pH to 8 and yield of tannins were higher when it was used in extractions (Figure 5). Urea increased the pH of the extract at 90 °C.

Based on lab scale results seemingly unrelated regression model was created to analyze effect of bark source, wood species, extraction temperature and chemical addition on extraction yield. Model shows that Stiasny no. decreases due increasing extraction temperature for spruce bark with pure water. Stiasny no. of pine bark decreases as the extraction temperature increases. Sodium carbonate seems to be the most promising chemical addition.

Task 2.3 Continuous extraction (Xamk)

Crushed pulp mill bark May-June 2018 from pulp mill was used in experiments.

The preliminary tannin extraction runs were carried out in pilot size continuous screw reactor shown in Figure 7. Length of the reactor vessel is approximately 2.2 m and the inner diameter is 0.34 m.

The average particle size of spruce bark was 0.5 mm (Figure 11). This bark fraction was separated from the original grinded bark sample by use of vibrating slope screen. The sieving was carried out to obtain bark that could be easily fed into the reactor by plug screw and also to optimize the particle size for enhanced mass transfer.

Figure 7 Continuous screw reactor

The runs were carried out using two different feed modes: a) eccentric screw pump b) plug screw pump (see Figure 8). Several reactor-feeding options were tested before the preliminary extraction runs. As a result of testing, normal pressure was chosen to ease running the adequate amount of liquid (water) through the reactor. Supplementary water was necessary for achieving the proper bark/liquid ratio when the plug screw pump was used. According to the test runs, this pump allows 25 % consistency of bark at the minimum. The supplement water was let into the reactor via separate pipeline next to the plug screw pump. When the eccentric screw pump was used the bark-water suspension was fed using funnel type vessel (Figure 8c). Air was fed below the screw axis. The airflow prevented clogging of bark at the feed point.

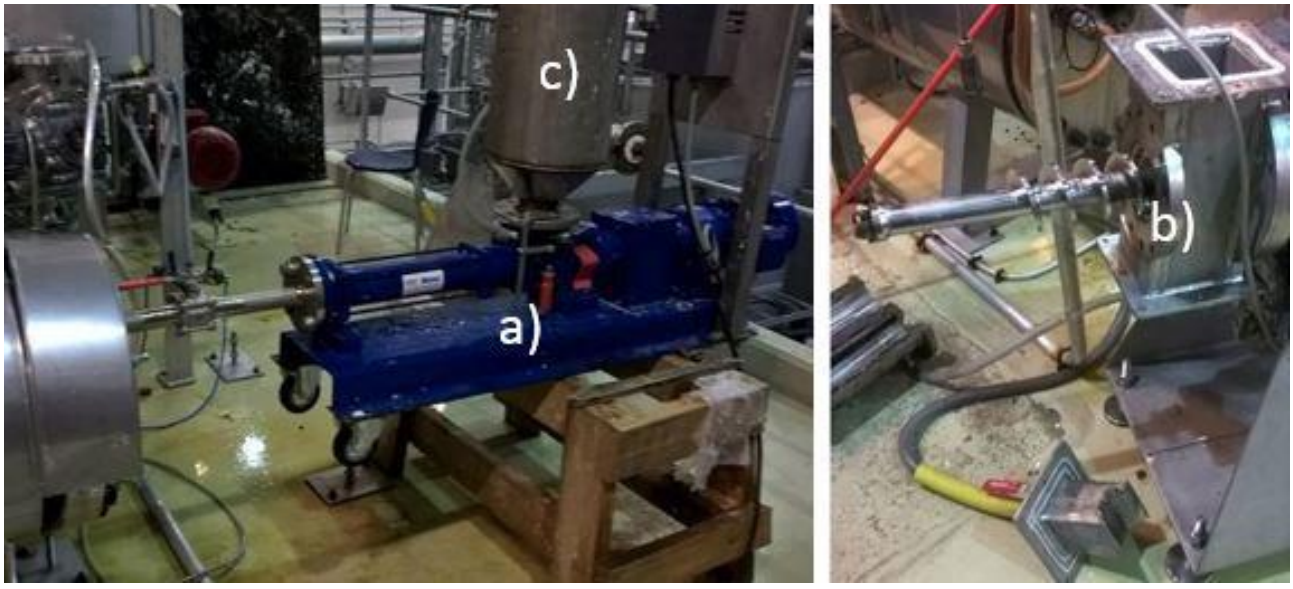


Figure 8 a) Eccentric screw pump b) Dismantled Plug screw pump c) Funnel type vessel

Preliminary run using eccentric screw pump

To ensure a successful reactor feed, a rather low (4 %) bark/water ratio was used. During the reactor feed tests it was found out that the high consistency of the bark water suspension tends to cause clogging at the entrance point of the pump. The lowered bark/water ratio should also increase tannin yield. The extraction temperature was approximately 80 °C. The temperature was maintained by vapor feed into the reactor. The mixing type screw (Figure 9) was used in the reactor to enhance mass transfer. The rotation rate of the screw was set for theoretical residence time of 20 minutes. The suspension feed rate was 0.43 kg/min. The tannin yield based on UV-spectrophotometer analysis of the extract was 2.1 %.

Figure 9 Mixing type screw

Preliminary run using plug screw pump

The consistency of the bark water mixture was 33 %. However, by the supplementary water feed 13 % bark/water ratio was maintained. The extraction temperature was approximately 85 °C. The temperature was maintained by vapor feed into the reactor. The mixing type screw was used in the reactor to enhance mass transfer. The rotation rate of the screw was set for theoretical residence time of 20 minutes. The feed rate presented as summed suspension mass flow was 0.9 kg/min. Some over flow of liquid takes place at the plug screw. That was taken into consideration for the calculation of the amount of water in the suspension. The tannin yield based on UV-spectrophotometer analysis of the extract was 2.5 %.

Tannin extraction using continuous screw reactor

Crushed pulp mill bark from pulp mill (sampled May-June 2018 and milled in an industrial setting) was used in experiments. In December 2018, the preliminary extraction test runs were carried out. The results showed, that the both tested feeding modes a) eccentric screw pump and b) plug screw pump can be used when suitable dry-water ratios are applied. For successful reactor feeding dry-water ratio 4% at the most (eccentric screw pump) or dry-water ratio 25% at the minimum (plug screw pump) are needed. The suspension dry-water ratio was adjusted using additional water feed at the feed end of the reactor.

Bark properties

The average particle size of the used bark was 0.7 mm (fraction 1, see Figure 10 and Figure 11). The extraction runs with fraction 2 and 3 were too difficult to carry out because of the wood sticks which caused clogging at the reactor feed. The water content of bark was 0.25 %. The bark was divided to three fractions using a vibrating slope screen of mesh size 6 mm.

Figure 10 Three fractions obtained by use of vibrating slope screen

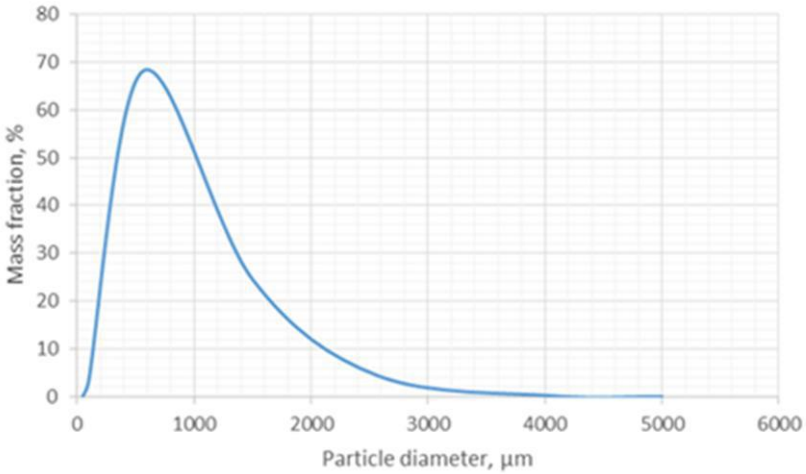


Figure 11 Particle size variation of screened bark fraction 1 used for experimental runs

Reactor operation parameters

Before each run the reactor was filled with water to the half of the reactor height and heated to running temperature. During each run the suspension level was kept constant at the half of the reactor height and temperature was adjusted with steam. The temperatures of the experiments were 80, 85 and 110 °C. The nominal residence times were 20, 50 and 100 min. The bark was soaked before each run with the soaking times of 1, 24, 48 and 96 h. At the feed point of bark, the used suspension dry-water ratios were 3, 4, 13, 26 and 75 %. In the case of the plug screw pump the additional water was fed at the feed end of the reactor to

adjust the bark-water ratio to desired value. Thus, the true bark-water ratios were 2.3, 3, 4, 8 and 16 % (Table 4).

Screw types

Most of the runs were carried out with modified mixing type screw or standard screw. A couple of runs were performed with mixing type screw. The screws used in the continuous screw reactor are shown in Figure 12.

Figure 12 The screw types used in continuous screw reactor during the experimental runs

Results of the experimental runs

Tannin content of the extract was analyzed using UV-Vis spectrophotometer for absorbance at 284 nm. The results of the experimental runs are shown in Table 4.

Table 4 Results of the experimental runs carried out with continuous screw reactor

Screw type	Soaking time	Temperature	Feeding mode	Suspesion flow rate	Nominal residence time	Dry-water ratio	Yield extract	Yield, phenolic compounds (tannin)
	h	°C		l/h	min	%	%	%
Standard screw	1	80	Eccentric screw pump	25,8	20	4	2,79	2,1
Standard screw	1	85	Plug screw pump	57	20	13	2,9	2,5
Mixing screw	1	110	Eccentric screw pump	164	50	3	4,5	2,7
Mixing screw	24	110	Eccentric screw pump	168	50	3	7	3,7
Mixing screw (modified)	Dry feed	110	Plug screw pump	184	50	2,3	2,9	1,8
Mixing screw (modified)	48	110	Eccentric screw pump	203	50	3	12,5	9,7
Mixing screw (modified)	96	110	Eccentric screw pump	203	50	3	17.0	11.8
Mixing screw (modified)	48	110	Eccentric screw pump	102	100	3	22.5	13.7
Mixing screw (modified)	96	110	Eccentric screw pump	102	100	3	14.0	11.6
Standard screw	48	110	Plug screw pump	102	50	16	2.5	1.5
Standard screw	48	110	Plug screw pump	160	50	8	3.8	2.3
Standard screw	96	110	Plug Screw pump	160	50	8	6.1	3.9

From Table 4 and Figure 13 it can be deduced that higher solid-water ratio produces lower yield. A longer soaking time seemed to be better than short, for obtaining higher yield (Table 4 and Figure 14 and *Figure*

15). The mechanism to obtain higher yield takes place probably by opening of the pore structure in the bark, enhancing mass transfer from the inner bark. According to data in Table 5, the longer nominal residence time does not seem to be advantageous for the higher yield. However, more data is needed to assure the effect on yield between the nominal residence times 50 and 100 min.

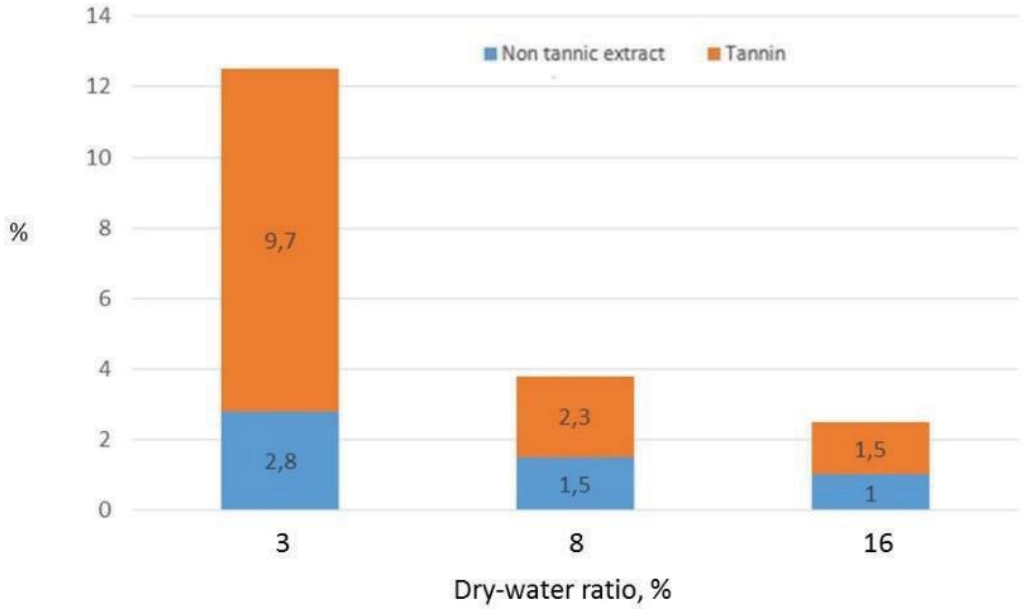


Figure 13 Yield percentages of extracts at different solid-water ratios. The pre-soaking time was 48h. The nominal residence time was 50 min.

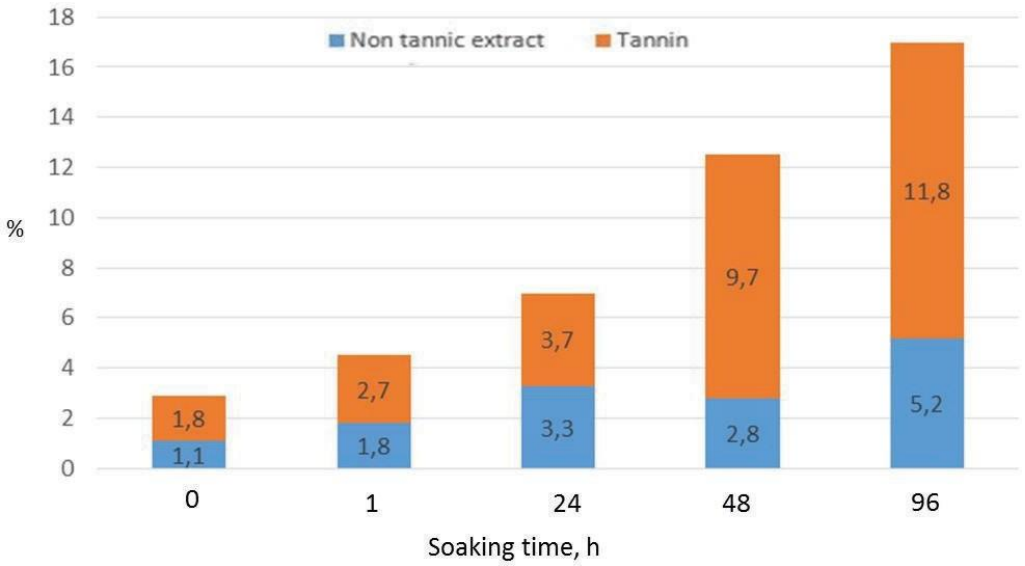


Figure 14 Yield percentages of extracts with different presoaking times of bark. Extraction temperature was 110 °C. The nominal residence time was 50 min. The dry-water ratio was 3 %, except with dry feed the dry- water ratio was 2.3 %.

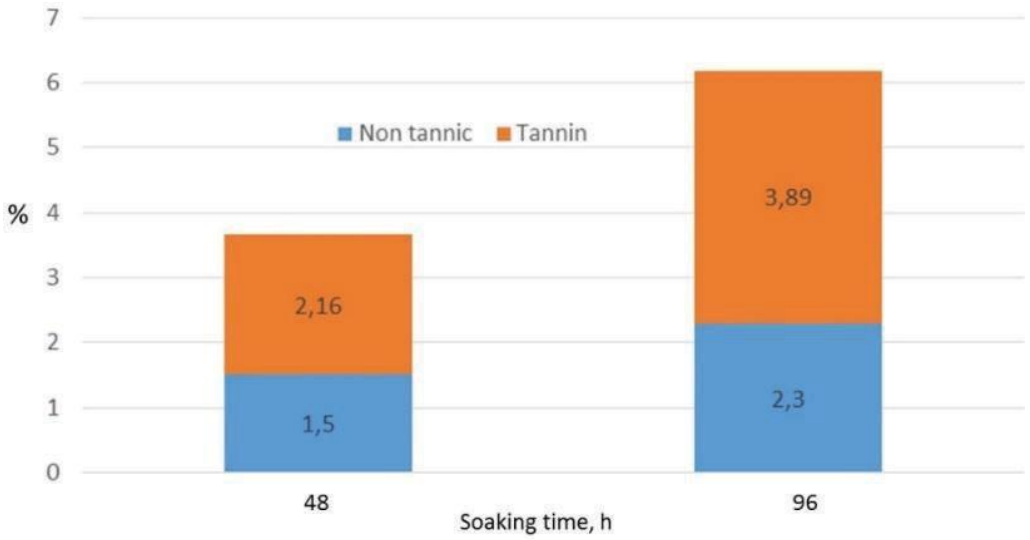


Figure 15 Yield percentages of extracts with different presoaking times of bark when plug screw pump was used. The dry water ration was 8%. Extraction temperature was 110%. The nominal residence time was 50 min.

Practically all soaking water by passes the feed point when a plug screw pump is used. This by passing is characteristic of when the plug is formed at the feed point. When plug screw pump is used for feeding, the positive effect of soaking may be reduced somewhat. That could come from the fact that at the feed point of the pump the bark is strongly compressed. This hypothesis needs some further experimental runs to be assured.

Conclusions

A longer soaking time seemed to be better than short, for obtaining higher yield. During four days preliminary soaking of 10 % bark-water suspension at 20 °C, only 1.4 % of the dry weight of bark is dissolved in the soaking water. Thus, during the preliminary soaking dissolved matter cannot explain all the better yield obtained in the analyses. At the feed point passed over flow of the feed liquid should be taken in to consideration when calculating the final yield of extraction in the case of plug screw pump. This would increase the presented yields some a what. The preceding soaking of the bark also minimized the mechanical feeding problems (clogging). If soaked suspension of about 3 – 4 % is used, a continuous feeding system with a storage tank would be easy to design because of the good handling properties of the suspension at that dry-water ratio. A higher yield is obtained with lower dry-water ratio that suggests, that the internal diffusion in bark does not determine mass transfer that much, as is the case without presoaking of bark. The use of plug screw pump may possibly take away some of the positive effect of presoaking by squeezing the pore structure. Because of the reactor being in daily industrial use, slightly different types of screws were used for practical reasons. The effect of screw type has not been taken in to consideration in this report and is beyond the scope of the current study.

Future tasks

Additional experimental runs are recommended to be carried out to ensure the effect of preliminary soaking of bark at high bark-water ratios. An eccentric screw pump and a plug screw pumps were feeding options in this research. However, another appropriate method for feeding bark-water suspension in

the reactor should be developed to be able to carry out comparable experiments at all possible dry-water ratios and at bigger particle sizes of bark.

Task 2.4 Up-scaling of the batch extraction process (Luke)

Raw material

Bark material for tannin extractions at the 300 l vessel was obtained from a pulp mill. Spruce bark was milled in an industrial facility. Bark was delivered to Bioruukki in a large container bag. Bark was very fine after grinding, but the wood content was also rather high in the samples (Figure 16). Sample was further named as MF-S3-M.

Figure 16 Bark sample MF-S3-M

Extraction system

Bark was extracted using 300 L pressurized hot water extraction unit as described in Figure 17.

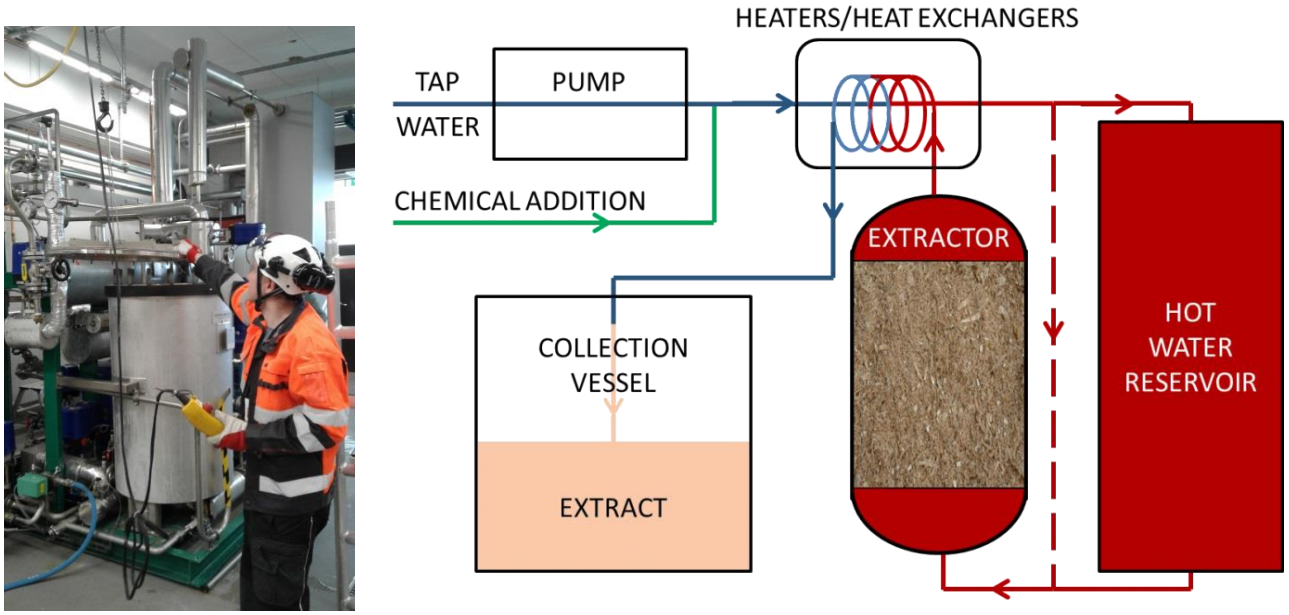


Figure 17 Extraction system and schematics

System can be used as a batch or in a flow-through mode. System is consisted of a pump, heat exchangers, a hot water reservoir and a collection vessel. Pressure range is 0 – 25 bar and temperature range 10 – 220 °C. Steam can be used to heat biomass before extraction. Spruce bark sample was extracted in batch mode.

Bark was extracted with hot water based on results from laboratory scaled extraction (Deliverable 2.1. Conditions for an optimal tannin extraction in batch process). Target extraction temperature was 110 °C for 120 minutes. A batch of 45 kg o.d.w spruce bark (60.64 kg fresh) was used in extraction (Figure 18).

Figure 18 Reactor filled with bark

Bark was added to reactor and system was heated by using 120 °C steam for 10 minutes with 1,8 kg/min steam flow. When heating phase was over, the reactor was filled with water at 115 °C. Temperature was measured inside reactor using altogether nine thermopairs that were inserted with steel pikes to the reactor. Temperature was higher and unevenly distributed at the start of extraction but it stabilized to an average extraction temperature of 106 °C (Figure 19).

Figure 19 Temperatures inside the reactor during the extraction

After two hours, the extract was cooled down in a heat exchanger and collected to a 1000 L container.

Results

A total of 252.4 kg of extract was collected in a 1000 L container (Figure 20).

Figure 20 Hot water extract in a container and extracted bark remaining in the vessel

The actual extraction temperature of 106 °C was close to the target conditions at 110 °C. Extraction proceeded smoothly, and extract could be readily collected.

Total dissolved solid (TDS) of extract was 1.28 %, in other words, 72 mg/g of original o.d.w bark was extracted. Theoretical overall extraction yield was 97 mg/g of dry bark. The pH of extract was 4.4.The amount of tannins and tannin reactivity were measured according to previously described methods (D 2.4 Procedures for determining polyphenolics, Stiasny-number and carbohydrates available for partners). The tannin content of the extract was measured by using UV spectroscopy and the wavelength at 280 nm. According to the results,

the theoretical tannin content measured with UV-method was 46 mg/g. Extract contained 29 mg/g of bark. A sample of extract was freeze-dried and Stiasny number of tannins was also measured. Stiasny number was 34.9.

Figure 21 Water balance of hot water extraction and water distribution between extracted bark and extract

The weight of the bark after extraction was 130.45 kg (average dry weight was 34.1 %) (Figure 21). If all water could be pressed out of bark, theoretical tannin yield would be 46 mg/g. Water in extracted bark contained 37 wt% of total tannins. Rest of the tannins, 63 wt % was in extract. Bark was more tightly packed after the extraction than before the extraction. It formed peat like mass that was fitted tightly inside the reactor. When the reactor was emptied by raising extracted bark upwards, sound of flowing water could be heard inside the pipes. It indicated that extracted bark formed uniform tight mass which acted like plug. The weight of bark increased during the extraction since water bark was wetted.

When results are compared with earlier lab scale extractions (D2.1), where extracts yield was 117 mg/g and tannin yield 36 mg/g, the yield of pilot scale extraction was lower, resulting 72 mg/g in total and 29 mg/g of tannins. Thus, the total yield was 38 % lower and tannin yield was 20 % lower than in laboratory scale extractions. In laboratory experiments, 70 ± 6 % of extract was collected. In pilot scale 74.1 % of extract was collected, which is larger amount than average laboratory scale experiment. However, total yield was lower in pilot scale than in lab scale.

This could be due the thickness of extracted bark bed, which could prevent bark to wet and slow down extraction. It would be better to have mixing or circulation in batch experiments. In further studies, a larger average particle size could improve the yield. Based on these results it would be important to mix bark during the continuous extraction in order to prevent bark to form clogs or dense bark bed that would reduce tannin extraction yield.

Heating value of extracted spruce bark

The heating value of spruce bark before and after extraction in pilot scale at Luke was determined to evaluate the effect on energy production. The analysis was performed for the bark fed to the pilot extraction (milled in and industrial facility, MF-S3-M) and the bark after extraction at Luke and pressing in an industrial setting.

The analysis results are shown in Table 5.

Table 5 Results from the determination of heating value for spruce bark from the pilot extraction at Luke.

Sample	Moisture	Dry	Ash	Hydrogen	Heating value		
					Gross calorific	Net calorific	Net calorific value as received
	%	%	%	%	MJ/kg	MJ/kg	MJ/kg
Bark extracted & pressed	0.23	99.77	4.98	5.7	19.742	18.499	8.869
Bark MF-S3-M	0.45	99.55	4.79	5.7	19.785	18.542	16.298

Gross heating value and net caloric heating values were similar before and after extraction and pressing. Since extracted and pressed bark had more moisture, net calorific value as received was lower than original bark. Both samples had similar ash and hydrogen contents. Results indicate that hot water extraction did not have any effect on gross calorific and net calorific heating values. The net calorific value of the extracted bark will increase after drying.

Conclusions

Spruce bark sample was extracted in pilot scale using a batch extraction system. Extraction conditions were very near the target conditions and extract was successfully collected. Theoretical tannin yield was 46 mg/g and extract contained 29 mg/g of original bark. Theoretical overall yield was 97 mg/g of which 72 mg/g was in extract. Extraction yield was lower than in laboratory scale experiments. This is probably due bark forming a dense plug-like bed in the extraction vessel and thus, lowering the extraction yield. Hot water extraction did not have an effect on gross calorific and net calorific heating values of bark.

Task 2.5 Analysis of the tannin fractions (VTT, Luke)

The methods used for the analysis of tannin fractions were collected to Delivery report 'D 2.4 Procedures for determining polyphenolics, Stiasny-number and carbohydrates available for the partners'. Additional information is given in the specific reports.

Milestones and deliverables

- **MS 2.1** Tannin extraction in batch process optimized (Month 14)

- **D 2.1** Conditions for an optimal tannin extraction in batch process (month 14) 15.1.2019
- **D 2.2** Procedure and processing parameters for tannin extraction in continuous process (month 24) 31.5.2020
- **D 2.3** Large batch of tannin produced with optimized extraction batch process (month 20) 14.5.2019
- **D 2.4** Procedures for determining polyphenolics, Stiasny-number and carbohydrates available for the partners (month 4) 25.10.2017

4. WP3. Fractionation of tannin

Task 3.1 Partial purification of crude tannin to obtain enriched tannin fraction (VTT)

The objectives of this part of the project was to enrich the content of phenolics from crude tannins of softwood bark. The approach included enzymatic treatment (enzymatic hydrolysis of oligomeric, polymeric and bound carbohydrates to monosaccharides), followed by membrane filtration in order to remove monosaccharides and obtain enriched phenolic fraction as shown in Figure 22.

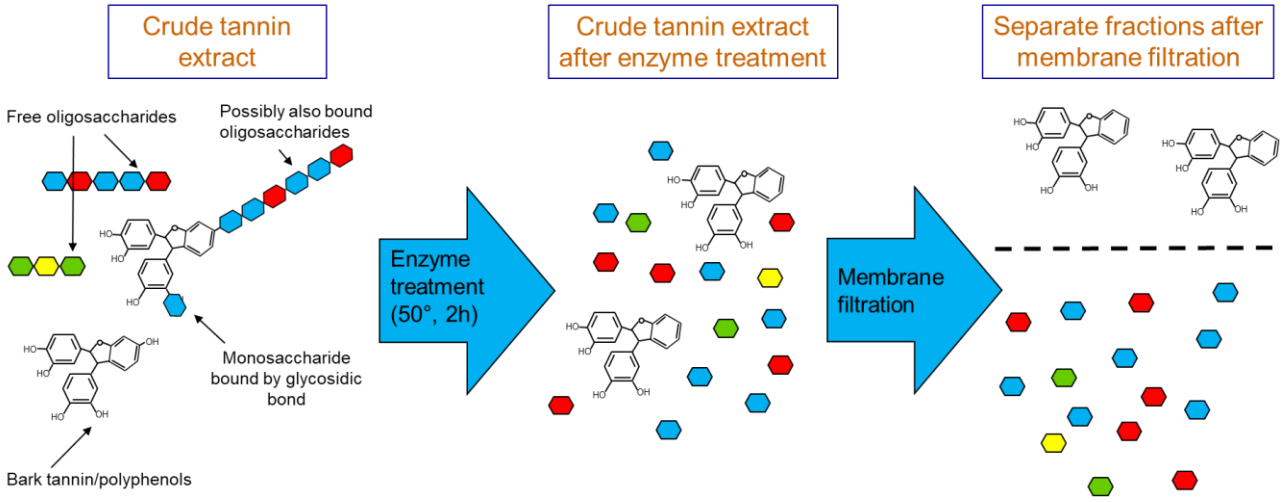


Figure 22. Concept for tannin purification by enzyme treatment

Screening phase

The performed work was started by **screening of enzymes** for their activity towards carbohydrates in crude tannin preparations (Biannual progress report Months 13 - 18, see Table 23). **Separation of monosaccharides from phenolics** with alternative approaches was then developed in small scale. The optimized protocol was upscaled using pilot-extracted crude spruce tannin (D3.1 report, see Table 23).

The **screening experiments** were performed with never-dried crude tannin extracts from the first saw mill bark (August 2017, batch 4. MF-S-M-1 for spruce and batch 3. MF-P-M for pine), as well as never-dried fresh crude tannin extracts from pulp mill bark (May-June 2018) (

Table 6). The enzymatic treatments were performed mainly in small scale (1-30 ml) and partly scaled up to bench scale (3 L) to provide samples for the development of the separation. Sugar release was measured with a method using 4-hydroxybenzoic acid hydrazide (PAHBAH).

Table 6. Crude tannin extracts composition for never-dried samples, calculated based on DM from bark extracts composition.

Batch	Starting material		Ph	Dm, %	Carbohydrates, %	Phenolics, %
2017	Spruce crude tannin	MF-S-M-1	4.5	9.7	34.9	42.0
	Pine crude tannin	MF-P-M	4.3	4.7	43.9	31.5
2018*	Spruce crude tannin	MF-S2-M	4.3	8.4	n/d	n/d
	Pine crude tannin	MF-P2-M	4.7	8.0	n/d	n/d

**- batch 2018 was not analysed for lignin/carbohydrate content, it was assumed to be similar to 2017-production.*

Commercial enzymatic preparations were provided by an industrial enzyme manufacturer based on results of preliminary trials (Table 7). The preparations contained mainly glucanase (EC 3.2.1.8(4)), pectinase (polygalacturonase EC 3.2.1.15) and pectin lyase (EC 4.2.2.10) activities.

Table 7. Tested enzyme preparations for hydrolysis of carbohydrates in crude tannin samples.

Commercial preparation number	Enzymatic activities*	EC	T, ˚C	pH	Substrate*
1	β-1,3-glucanase β-1,6-glucanase	3.2.1.8 3.2.1.4	35-70	3-7	non-starch β -glucan
2	pectinase arabinase	3.2.1.15	20-60		soluble pectin insoluble pectin
3	pectinase arabinase	3.2.1.15	30-55		pectin arabinan
4	pectinase arabinase	3.2.1.15	20-55		pectin hemicellulose
5	pectin lyase	4.2.2.10	20-50		pectin

* - according to the product data sheet

Enzymatic preparations were tested in hydrolysis reactions with crude tannins in wide pH range. The most efficient preparations were:

- No 3 (major enzymatic activity – polygalacturonase, EC 3.2.1.15)
- No 4 (major enzymatic activity – arabinase, EC 3.2.1.15)
- No 5 (major enzymatic activity pectin lyase, EC 4.2.2.10).

Since enzymes cost makes a large impact into final product price, trials of enzymatic treatment optimization were performed in order to reduce enzyme consumption. While searching for optimal conditions following factors were examined:

a) variation of enzyme dosage;
b) variation of enzyme loading (addition of the enzyme at once or stepwise);
c) addition of surfactant polyethylenglycol (PEG);
d) variation of DM % w/v in hydrolysis reaction;
e) variation of the temperature.

Different dosages were tested in crude tannin hydrolysis (Figure 23). Sugar yields did not increase significantly with increase of enzyme dosage, thus the substrate seemed to be a limiting factor. Enzymatic dosage of 5 mg was chosen as an optimal in terms of enzyme consumption – carbohydrates yields ratio. Preparation no. 3 was shown to be better for pine, while preparation no. 4 was better for spruce crude tannin hydrolysis.

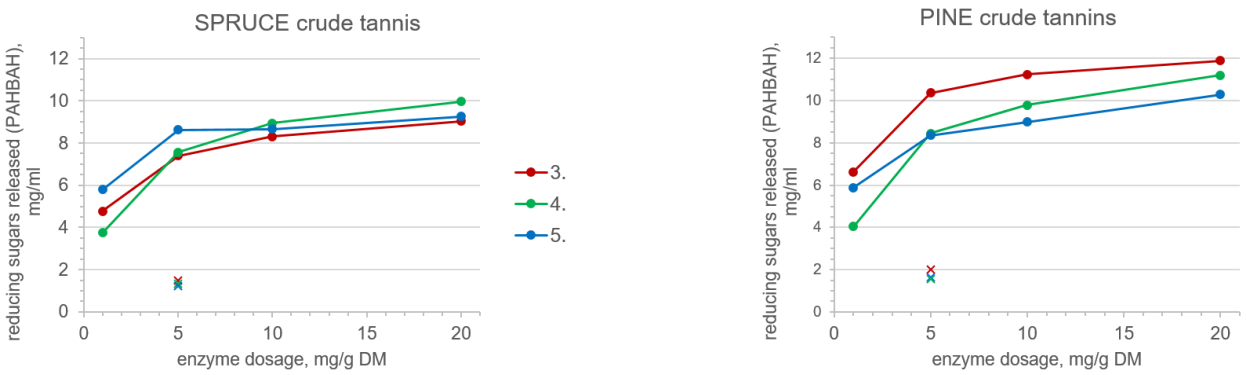


Figure 23. Variation of enzyme dosage. Hydrolysis of crude tannins was carried out at 50˚C in NaAc buffer pH 5.0 for 2 h, stirring at 800 rpm with variable enzyme dosage 1-20 mg per 1 g DM using enzyme preparations 3-5. Crude tannin DM in reaction was 2.5%, bark batch-2017. Due to variation in bark batches repeating experiments for a fresh crude tannin extracts (2018) gave much lower carbohydrate yields – marked "x" on the plot, colored accordingly.

The strategy of continuous addition of the enzymes was revised with the new batch of enzymes since protein precipitation by tannins is a well-known phenomenon. However, the addition of the enzyme at once or stepwise did not affect the carbohydrate yields in hydrolysis reaction. Another approach was to reduce possible enzyme precipitation by the presence of a surfactant (polyethylene glycol, PEG). This surfactant is known to reduce precipitation of enzymes by lignin. In case of crude tannins enzymatic hydrolysis PEG 2000 and PEG 4000 were used in dosage 5-42 mg per 1 g DM or 0.013-0.018 g per 1 g phenolics (rough estimation). At these particular conditions, the presence of surfactant had no significant effect, since enzyme precipitation mechanism of tannins might be different from lignin and needs further investigation.

Pilot production hot water bark extracts normally contain 1% DM. It was also suggested to perform treatments at a temperature of 50°C instead of room temperature as that is more realistic in industrial environment. Therefore, enzymatic hydrolysis tests with variable DM % w/v were performed at 50°C before upscaling. The results were consistent and showed optimal DM in range of 2.5-1% w/v at a temperature of 50˚C.

Further tests in slightly larger scale were performed to study combined activities of enzymatic preparations (Figure 24). The most promising combinations were pectinase + pectin lyase + glucanase for spruce and pectinase + pectin lyase for pine (Figure 24). Noticeably total enzyme dosage seemed to be limiting factor for sugar yield, still combined activities mixture was chosen for bench-scale samples preparation in order to cover different types of linkages cleavage in carbohydrates present in crude tannins and hopefully better access to tannins.

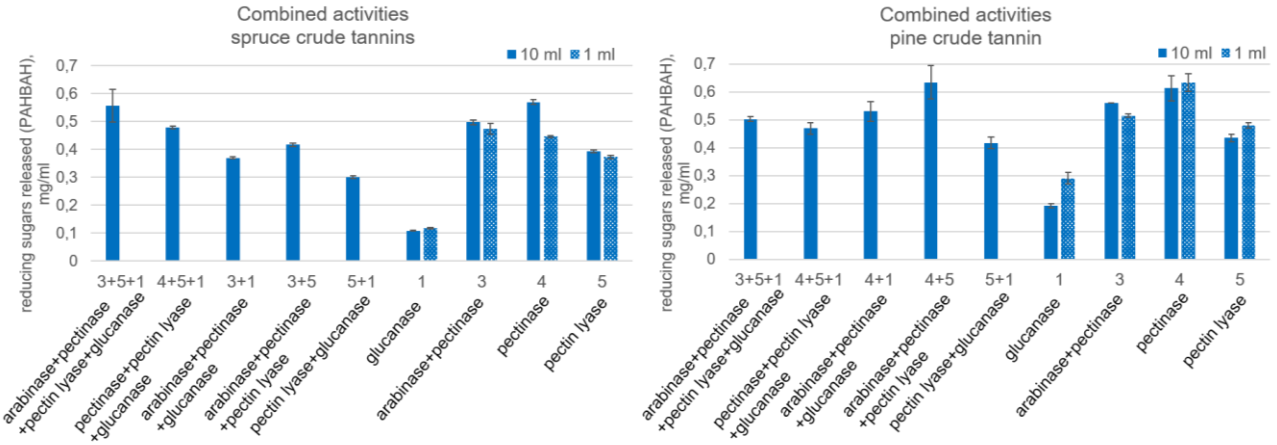


Figure 24. Combined enzymatic activities in crude tannins hydrolysis. Hydrolysis reaction was carried out at RT, 2 h, pH 5.0; enzyme dosage (total) 5 mg per 1 g DM, enzyme ratio in combination 1:1:1 or 1:1. DM in reaction 1% w/v, bark batch-2018 crude tannins were used. Enzymatic preparations are numbered according to Table 7. About 20% sugars of total sugars were hydrolysed at maximum.

More detailed study on enzyme dosage was carried out in combined activities tests with spruce tannins (Figure 25). Increase of combined activities dosage from 5 mg to 10 mg per 1 g DM did not give proportional response in sugar yields, while increasing preparation no. 4 alone dosage had bigger effect on hydrolysis yields at the same conditions. Thus an assumption was made that at 5 mg per 1 g DM dosage, a combined mixture should be more efficient than enzymatic preparation alone. For the pilot scale trial, a mixture of the preparations with pectinase and pectin lyase supported by glucanase activity was selected.

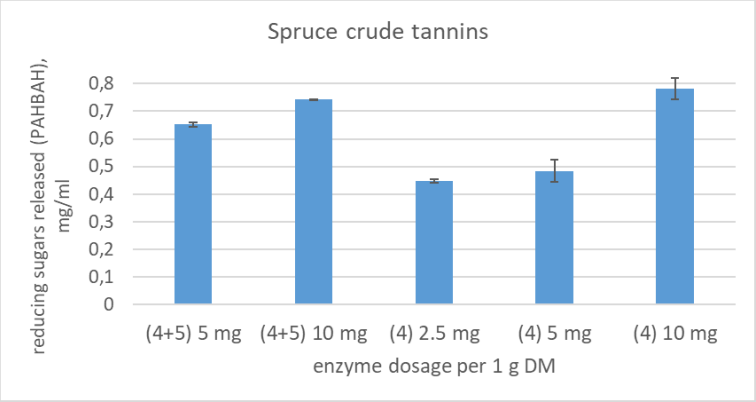


Figure 25. Combined activities in spruce crude tannin hydrolysis. Hydrolysis reaction was carried out at RT, 2 h, pH 5.0, DM 1% w/v, bark batch-2018 crude tannins were used, reaction volume 30 ml. Enzymatic preparations are numbered according to Table 7.

For the ***development of membrane fractionation***, samples of spruce and pine crude tannins (2018), 1% DM w/v (30 g DM tannins) at pH pH ~5 were treated in several liter scale with enzyme mixture of (1,4 and 5) using dosage 5 mg per 1 DM (150 mg enzymes, mixed in ratio 2:2:1). Hydrolysis was performed during 3 h with gentle mixing at RT (22˚C). pH adjustment was performed on the one hand to increase the solubility of tannins (pH 9 and pH 12) and on the other hand to enhance precipitation (pH 2 and 5) (Figure 26). All the details are available in the Biannual progress report Months 13 - 18 (Table 23).

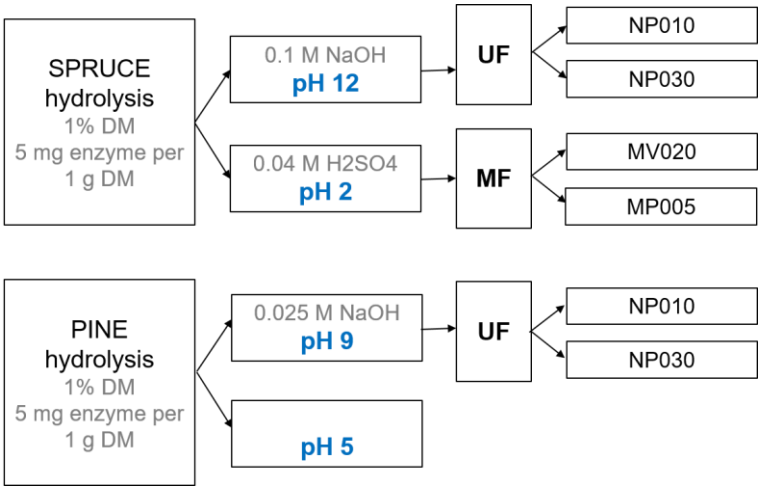


Figure 26. Scheme of membrane testing strategy applied to enzymatically treated spruce and pine tannins. UF – ultrafiltration, MF – microfiltration; membranes shown on the right side, specification Table 8. The sample adjusted to pH 5 was not further tested due to weak results for pH 2.

The **membrane screening for tannin concentration and purification** from monosaccharides and salts was carried out using a Millipore filtration test cell (Figure 27). Agitation was used for increased shear on membrane surface for fouling prevention in a dead-end filtration system. Membrane selection in a range from microfiltration to nanofiltration was done due to complex nature of wastewater stream and substances therein. The effective membrane area in the Millipore device was 30 cm^2, maximum batch volume 300 ml, and driving over pressure created by air, with maximum pressure of 6 bar. New membranes were used in all experiments. The membranes were kept in de-ionized water overnight for removing the possible preservative and dust from the membrane surface. Pure water flux (de-ionized water) and salt rejection, if

informed by manufacturer, before each experiment for membrane verification was measured. Due to extreme pHs of the tannin samples, membrane materials were selected to tolerate extreme pHs, i.e. polyvinylidene fluoride (PVDF, tolerates pH 1-12), and polyethersulphone (PES, tolerate pH 0-14) (Table 8).

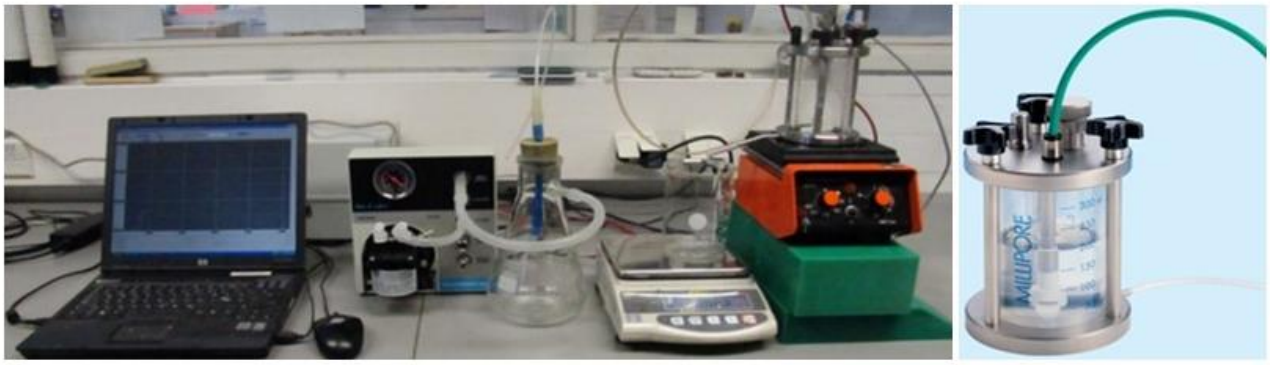


Figure 27 Millipore filtration test cell

Table 8. Membranes used in the prestudy.

Membrane	Material	Pore size	Permeability, lmh/bar		NA_2SO_4, rejection, %	
			Announced by manufacturer	Measured	Announced by manufacturer	Measured
MV020	PVDF	0.2 µm	>700	5500		
MP005	PES	0.05 µm	>285	1660		
NP010	PES	1000 -1200 Da	>5*	9±3**	35-75*	62±4**
NP030	PES	500-600 Da	>1*	2.1±0.1**	80-95*	73±3**

*Measured at 40 bar, ** Measured at 6 bar

The tests at pH 2 with enzymatically treated spuce crude tannin were based on the assumption that the phenolic tannins would precipitate and could be retained by the selected microfiltration membranes. The more open membrane, i.e. MV020, produced double permeability, less colourful permeate (Figure 28). The phenol rejection was lower for MV020 (58%) than for the MP005 membrane (66%). The rejection rate was nevertheless in both cases too low to separate the majority of the phenolics from monosaccharides. Carbohydrates passed the membrane to more that 86%.

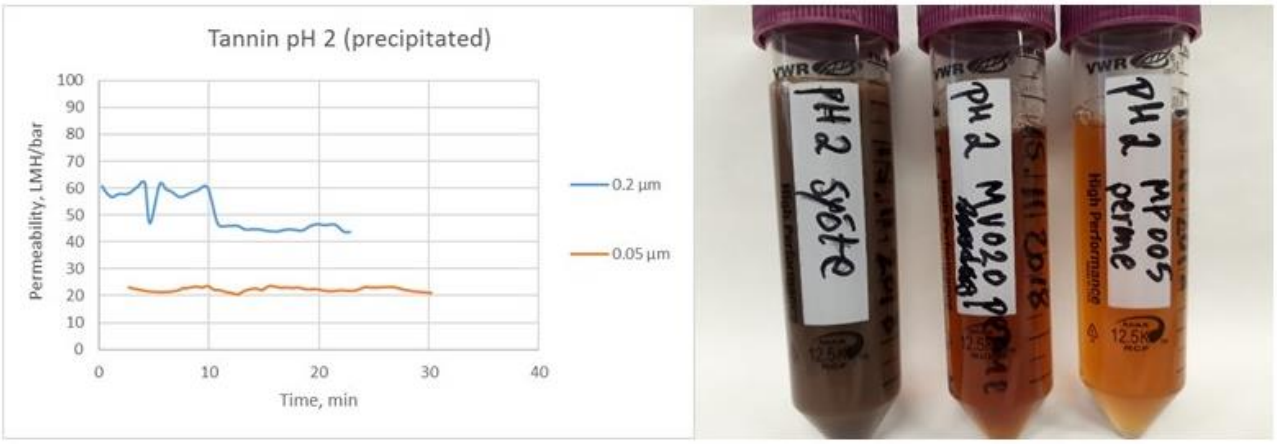


Figure 28 Permeabilities for the microfiltration membranes and spruce tannin sample at pH 2 (left). Pictures of feed and permeates of the spruce tannin sample at pH 2 (right).

Low permeabilities, clear permeates, especially NP030 permeate, and good rejections were obtained for spruce tannin extract at pH 12 using the both nanofiltration membranes (Figure 29). The permeability of NP010, i.e. 3.3 LMH/bar, was one tenth of the most open membrane, MV020, and more than three times higher than for NP030 membrane. Phenol rejections were 94% and 98% and carbohydrate rejection measured as Brix value 43% and 46% for NP010 and NP030 respectively.

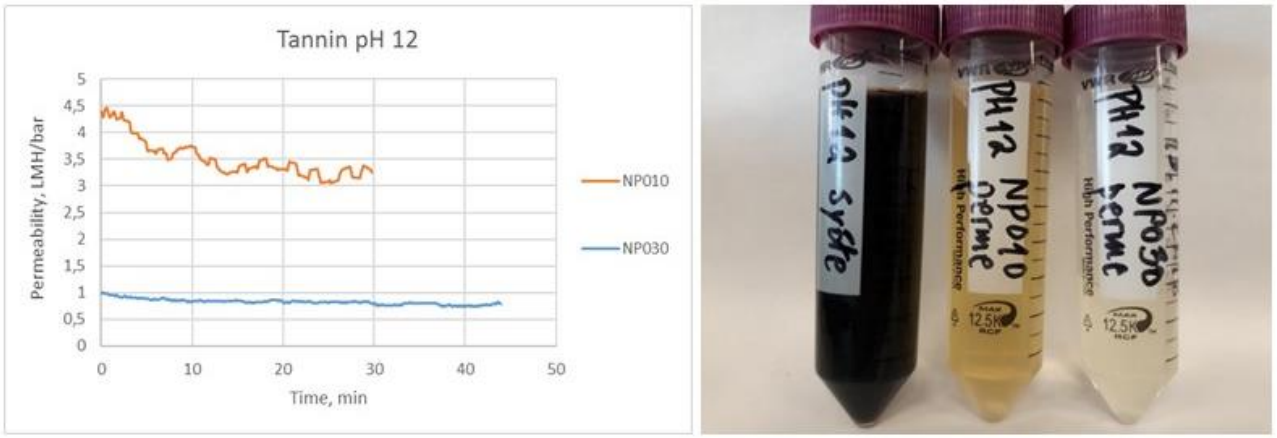


Figure 29 Permeabilities for the nanofiltration membranes and spruce tannin sample at pH 12 (left). Pictures of feed and permeates of the spruce tannin sample at pH 12 (right).

Low permeabilities, very clear permeates, and good rejections were obtained for pine tannin extract at pH 9 using the both nanofiltration membranes (Figure 30). The permeabilities were lower for the pine tannin sample at pH 9 than for the spruce tannin sample at pH 12 although phenol concentration in the feed was lower. Phenol rejections were similar, 94% and 97%, and carbohydrate rejections (Brix) a bit higher, 44% and 52% for NP010 and NP030 respectively.

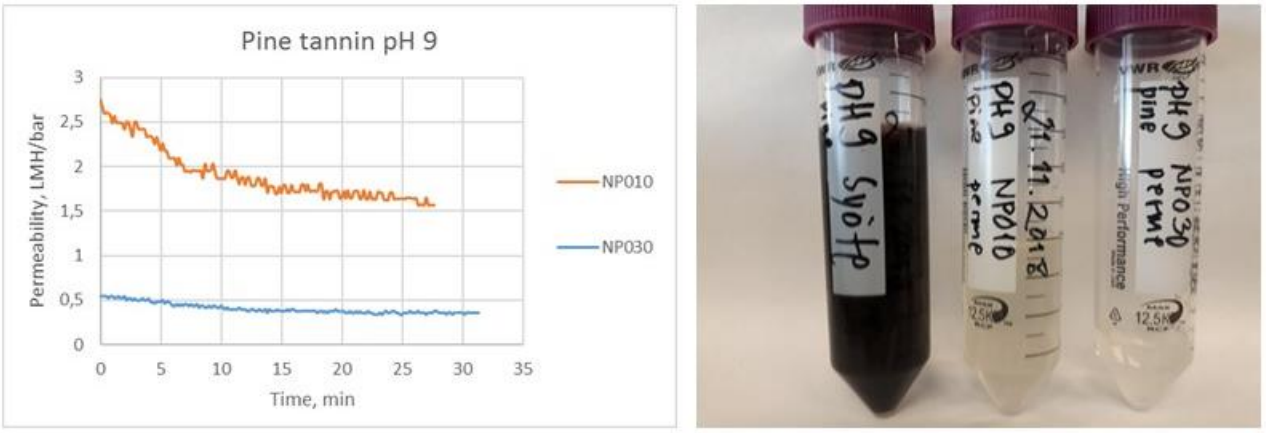


Figure 30 Permeabilities for the nanofiltration membranes and pine tannin sample at pH 9 (left). Pictures of feed and permeates for the pine tannin sample at pH 9 (right).

Based on the screening tests, low pH combined with microfiltration of precipitated tannin was rejected as a concept due to too low phenol retention. The nanofiltration results showed good phenol retention at pH 9 and pH 12. **For pilot nanofiltration, nanofiltration at pH 9 was selected**. The flux was higher at pH 12 but pH 9 was favored due to the moderate dosage of NaOH for reaching that pH.

Pilot trial

The pilot hydrolysis of the crude spruce bark hot water extract was performed at Bioruukki (see Task 2.4) facilities in three batches, all the batches were treated equally. In total, 50% of carbohydrates were liberated with enzyme dosage of 10 mg/g DM (Figure 31).

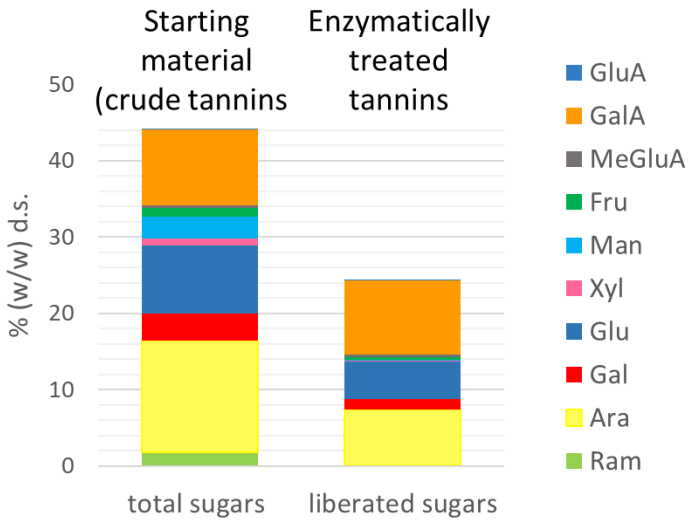


Figure 31. Total compared to liberated monosaccharide of spruce crude tannins. Total sugars were analyzed with HPLC after acid hydrolysis, including only neutral sugars. Acidic sugars were analyzed with HPLC only in enzymatically treated tannins along with neutral sugars.

The major carbohydrates released were galacturonic acid, arabinose, glucose, galactose, methyl glucuronic acid and fructose. Galacturonic acid normally constitutes the backbone of pectins, while arabinose might be

a part of arabinan or pectic galactan. The overall yield of liberated sugars was quite promising and thus the upscaling of the hydrolysis was successful. The selected commercial enzyme preparations are typically used in grape processing and advanced maceration of pome fruits, especially targeting grape skin which is rich in tannins. Probably the resistance of the enzymatic cocktails to precipitation by tannins was a key characteristic for a successful enzymatic treatment of spruce bark extracts. Nevertheless, more efficient enzymes with reduced cost are still needed to cleave off sugars from tannins in particular for a feasible industrial application.

The enzymatically treated spruce bark extract was fractionated by a sequence including pre-treatment, membrane fractionation and spray drying (Figure 32). Pretreatment was done using a cartridge MF, with 5 µm nominal pore size. Concentration of MF filtrate was carried out by a spiral wound NF element NFG-3-2540HM (Synder Filtration, USA) having MWCO of 600-800 Da. Its effective membrane area is 1.95 m^2, maximum operation temperature 50°C, and pH range at max temperature 4 - 9. NFG membrane was tested with 2000 ppm $MgSO_4$ salt for rejection prior to fractionation, resulted as 48%, which was close to the manufacturer's information of average $MgSO_4$ rejection of 50%.

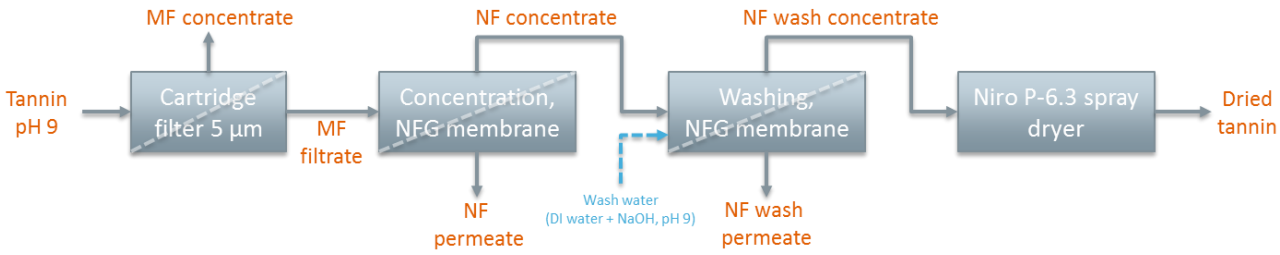


Figure 32. Fractionation scheme.

A cartridge filter was used to remove solids before the nanofiltration including some additional solids formed due to the intermediate storage in the freezer followed by defreezing. The nanofiltration was performed at pH 9 including the washing stage to ensure solubility throughout the filtration.

The NF concept using NFG spiral wound membrane consisted of tannin concentration and then washing of that concentrate by adding deionized water (pH adjusted to 9 using NaOH) at about the same rate as permeate flux. Figure 33 shows the permeate flux during concentration (a), concentrate washing (b), and °Brix decrease during concentrate washing (c).

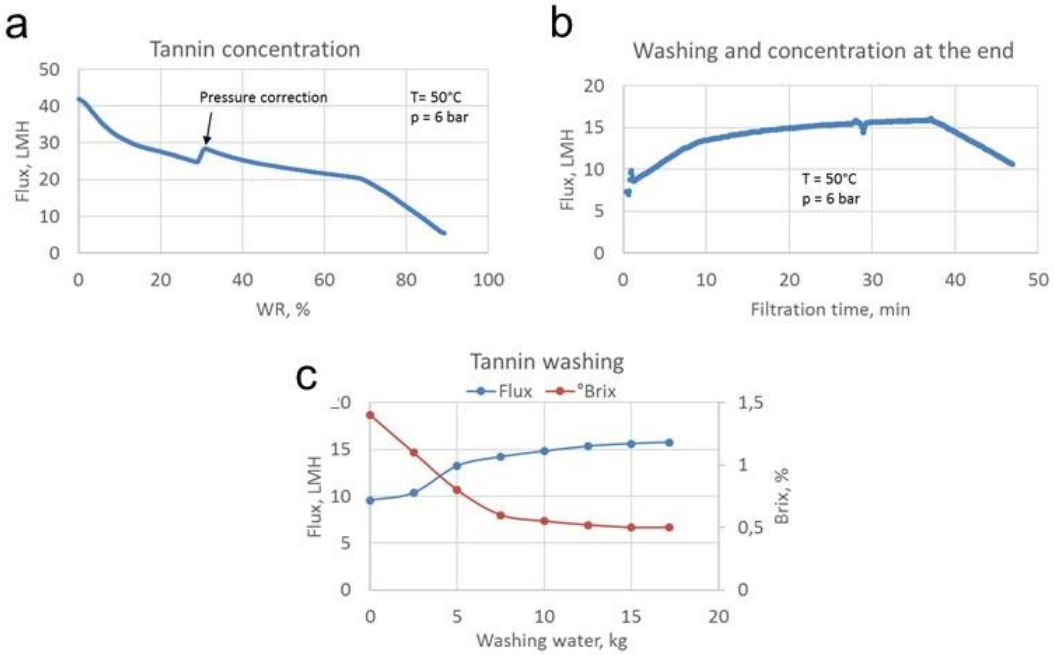


Figure 33 Parameters in membrane filtration of hot water extracts a) nanofiltration flux in tannin concentration b) washing stages, and c) with Brix values during concentrate washing

Fractionation of tannins using spiral NFG spiral wound element enabled to concentrate the treated crude tannin 9-fold. The membrane had good initial permeate flux of 40 LMH, and 5 LMH at high WR of 90%. The washed NF concentrate was spray dried yielding a product of 96% dry solids.

The analysis results of the most important samples are collected to Table 9. A high amount (14%) of total dry matter was removed in the cartridge filtration stage and large part of the dry matter was found to be tannin (54%). Freezing of the starting sample prior to filtration may have caused precipitation which was seen as yield loss. The liberated monosaccharides were removed successfully during NFG-concentration step, resulting in enriched phenolic fraction, i.e. NFG concentrate (Figure 34). However, also the permeate contained some phenols. Thus, both monosaccharides and low molecular weight phenols can pass through NFG membrane. Consequently, loss of phenols in the cartridge filtration stage, final washing and concentration step resulted again in a relative reduction of phenolic content in the final fraction (NFG wash concentrate). 57% of the phenolics fed to the fractionation were recovered in final NFG wash concentrate and 15% in cartridge filtration step. An increase of the average molecular weight was observed when comparing the starting material and the final washed concentrate (NFG wash concentrate) (Figure 35). The process has not been optimized and thus there is still space for optimization.

Table 9. Sample amounts and their analysis during fractionation.

#	Sample description	Fraction amount kg	Ph	Conductivity ms/cm	Total solids g/l	Tannins[1] g/l	Total sugars[2] g/l	Free sugars[3] g/l
1	Hot water extract		4.6		11.9	6.8	5.26	0.46
2	Spruce tannin pH 9 (enzymatically treated, feed to cartridge)	100.5	8.6	6.4	18.0	4.9	5.15	2.91
2C	Sludge from containers and cartridge filtration	2.7	8.9	6.3	54.9	26.5	8.22	0.95
2B	5 µm cartridge filtrate	96.3	8.6	6.4	16.2			
3	NFG concentrate	10.0	8.4	12.9	85.4	33.6	27.02	
4	NFG permeate	85.8	8.6	4.9	8.1	0.2	1.08	
6A	NFG wash concentrate	8.9	8.2	8.7	84.8	31.5	30.85	6.92
5	NFG wash permeate	17.6	8.3	4.3	6.2			
6B	Spray dried tannin	0.5						

[1] Tannins were estimated using UV-absorbance values at λ=280 nm and calibration curve with commercial tannin as a reference.
[2] Total sugars were measured after acid hydrolysis with HPLC.
[3] Free sugars were monosaccharides measured as such with HPLC.

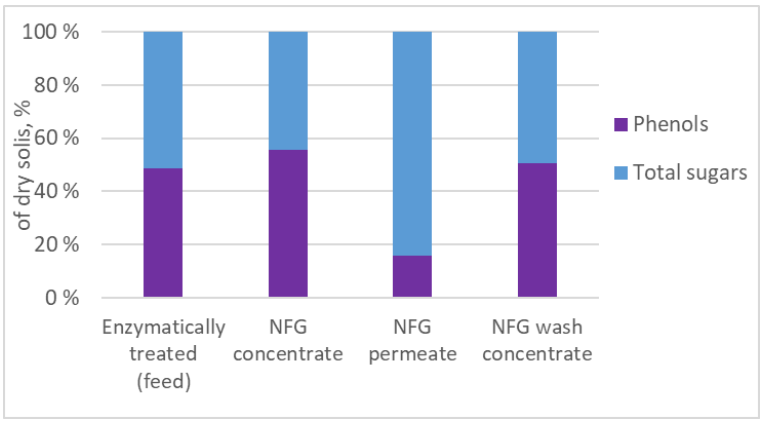


Figure 34. Composition of tannin fractions.

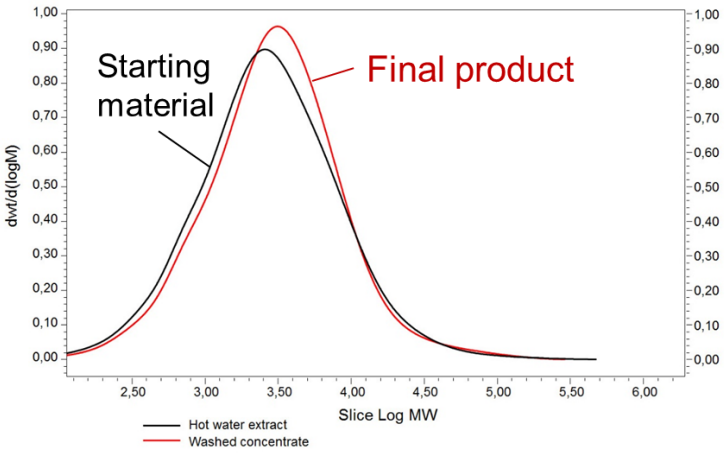


Figure 35. Molecular mass distribution in starting material and final product after fractionation. As expected, the Mw distribution of the final product was shifted to larger molecular weights compared to the starting material.

Task 3.2 Increase stability of tannin in aqueous solution (VTT)

Information on storage stability of the bark hot water extract (tannin) is essential for the industrial exploitation. Drying of tannin products consumed substantial amounts of energy and this increases the environmental impact (See Chapter 7 and WP6 data). Supply of concentrated aqueous tannin products could be reasonable in some cases.

The stability of bark hot water extracts was assessed during a 7-month storage period at +4°C by evaluating microbial growth and by measuring chemical reactivity with formaldehyde. Two concentrations were tested. The hot water extracts were found to be prone to microbial spoilage when stored at ambient temperatures.

The pH in the cold-stored extracts remained rather constant over the storage period, indicating that radical microbial growth of e.g. lactobacilli has not taken place. Against the original hypothesis, the hot water extracts were found to retain their reactivity with formaldehyde during the 7-month storage period (

Table 10). Turbidity of the samples was measured and a clear trend of increasing turbidity with increasing storage time was observed. This indicates that the extracts are not stable colloids. Some compounds may precipitate out from solution during storage and form more and bigger aggregates that are capable to scatter light in the turbidity measurement. The increase in turbidity was more pronounced in the concentrated solution.

Table 10 Reactivity (Stiasny number), weight average Mw, turbidity and pH of hot water extracts stored at +4°C over a period of 7 months.

Storage time months	Sample	Stiasny number	Mw (kda)	Turbidity	pH
0	Crude bark extract (11.9 g/L)	36.1	4,5	200	4.4
3		NA	NA	300	
7		37.8	5,7	400	4.0
0	Concentrated crude bark extract (29,8 g/L)	36.6	5,0	380	
3		NA	NA	410	
7		43.3	3,4	650	4.5

It may thus be concluded that any chemical sites that are relevant for formaldehyde reactivity are retained during wet storage without any chemical addition. Therefore testing of chemicals for improving chemical stability was neglected. However, preservatives to suppress microbial growth in aqueous solutions of bark hot water extracts should be considered if storage at room temperature has to be assured.

Milestones and deliverables

- **MS 3.1** Optimal membranes and filtration techniques evaluated (month 15)

- **D 3.1** Purification of a larger batch of crude tannin to obtain enriched tannin fraction (month 28) 28.10.2019
- **D 3.2** Report: Chemicals to improve tannin stability discovered and method for wet storage of tannin developed (month 28) 8.10.2019

5. WP4. Adhesive formulations

Task 4.1 Tannin-wood-adhesives for plywood and laminates (VTT)

The goal of Task 4.1. was to evaluate tannin for replacement of phenol in wood resins for wood gluing. In the beginning of the project, this was specified for replacement of phenol in phenol-formaldehyde (PF) wood resins for plywood gluing.

In PF wood resins, gluing performance is based on physical interactions as formaldehyde reacts to ortho or para- positions of phenols and forms methylene bridges between them. Moreover, formaldehyde reacts similar way with lignin present in the wood being glued. As a result, a hard covalently bonded 3D polymer network is formed between resin and wood.

The study included several project tannins and following steps:

- Evaluation of sodium hydroxide (NaOH) consumption
- Development of the hydroxymethylation phase in the wood resin synthesis
- Synthesis of the wood resins using different replacement levels and cooking conditions
- Testing of the wood resins in plywood gluing using a laboratory testing device (Automated bonding evaluation system, ABES)

NaOH consumption to reach pH 10 - a relevant pH for subsequent hydroxymethylation - was evaluated for crude tannins and reference tannins as shown in Table 11. The crude tannins from the softwood bark consumed less NaOH than commercial tannins. This is explained by the lower amount of phenolics in the softwood crude tannins compared to commercial tannins from other origin. This can also be seen an advantage because of saving in chemical consumption.

Table 11. Consumption of alkaline in pH regulation.

Tannin	Source	Phenolic content, % of dry weight	NaOH consumption to reach pH 10, mmol/g dry sample
Spruce crude tannin (MF-S-S from pilot trial)	VTT	40-50	2.5
Pine crude tannin (MF-P-S from pilot trial)	VTT	25-35	3.0
Fintan op	commercial	75.4	4.6
Fintan q	commercial	78.7	4.6

In the hydroxymethylation, formaldehyde is reacted with the tannin to measure the maximum formaldehyde consumption of different tannin extracts (mmol/g). The tannins were treated with 8 mmol formaldehyde / g tannin at pH 9-10 for 4h with the exception that Fintan was treated with a double dosage (16 mmol formaldehyde / g tannin). Two different temperature programs were tested differing in the initiation time of temperature increase and the duration of temperature increase as presented in Figure 36. The consumption was in line with the content of phenolics (Table 12, Figure 37).

- The crude spruce tannin consumed more formaldehyde than crude pine tannin.
- The commercial tannins consumed considerably much more, as expected.

Most of the formaldehyde was consumed during the first hour.

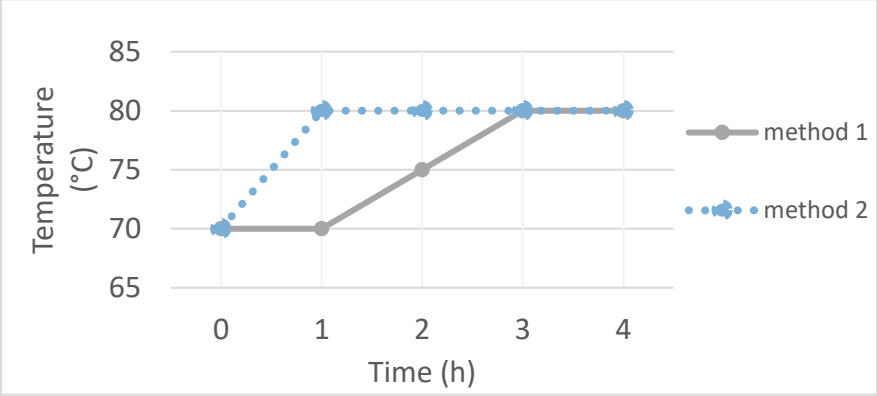


Figure 36 Temperature programs in the hydroxymethylation trial.

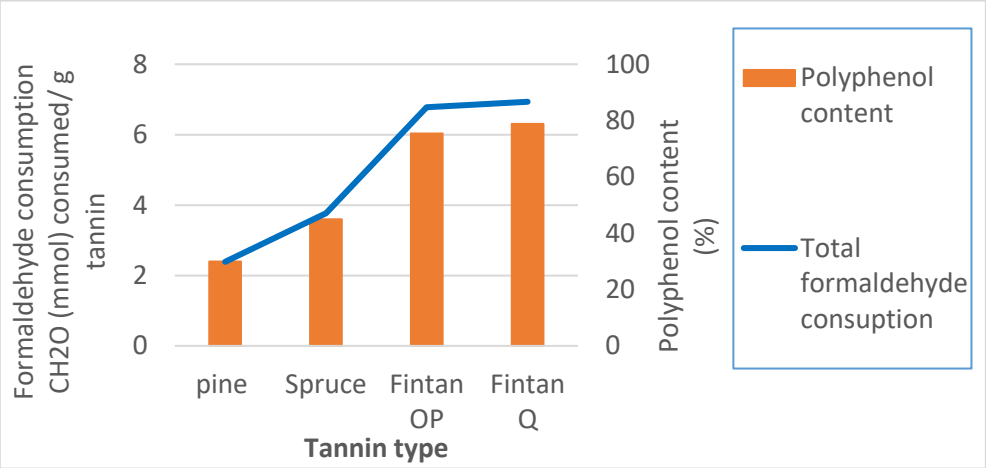


Figure 37. Total Formaldehyde consumption per tannin. Pine and spruce refer to the crude tannins according to Table 12.

The resin synthesis was performed by reacting the tannin with formaldehyde and phenol in alkaline condition. The reaction was performed in several phases as presented in Figure 38:

1. Liquid preparation meaning dissolution of the tannin to NaOH and formation of phenolate ions.
2. Formaldehyde addition for the hydroxymethylation of the tannin.
3. Addition Phenol and NaOH to activate the phenolics for crosslinking hydroxymethylated tannin and phenol.
4. Formaldehyde addition for crosslinking of the hydroxymethylated tannin and phenol.
5. Cooking to finalize the crosslinking reaction at a suitable phase. ‘

The performed trials are collected in Table 12. The cooking was evaluated in terms of cooking time and viscosity level.

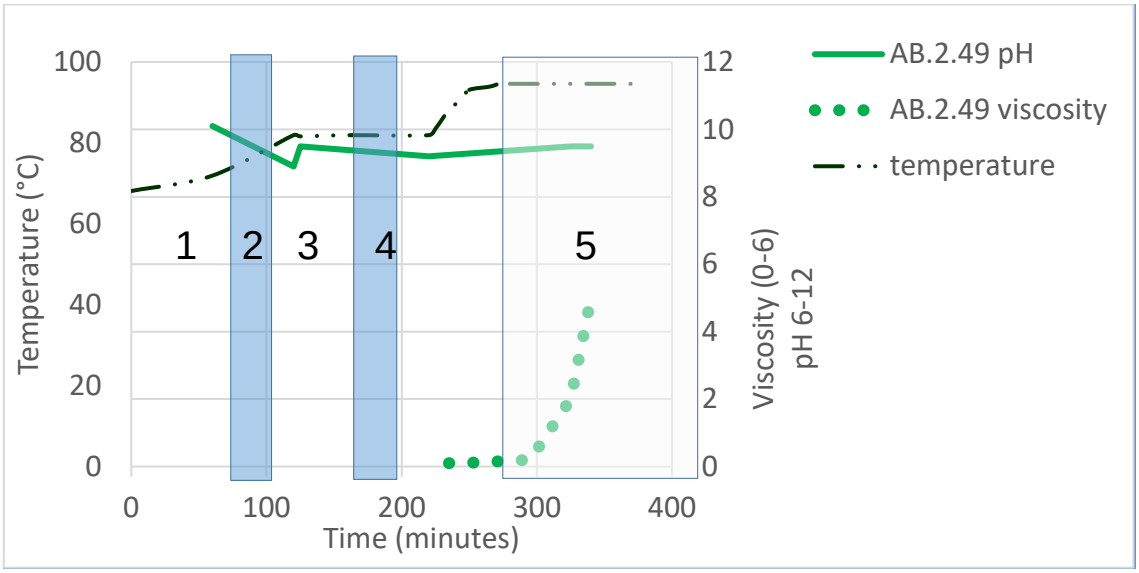


Figure 38. Visual representation of resin formulation method. (1) Liquid preparation, (2) Formaldehyde addition, (3) Addition Phenol and NaOH, (4) Formaldehyde addition, (5) Cooking. The AB number refers to entries in the laboratory notebook.

Table 12. Parameters in the wood resin preparation trials.

Replace-ment level	Tannins	NaOH/ tannin	Solids content	Formalde hyde/ tannin	Phenol	NaOH/ phenol	Formaldehyde /phenol)
%	molar eq.	eq.	%	eq.	eq.	eq.	eq.
50	1	3	40	4,2	1	0,4	1,5
50	1	3	40	4,2	1	0,2	1,5
50	1	3	40	4,2	1	0,2	1,5
30	1	3	40	4,2	2,3	0,4	1,5
30	1	3	40	4,2	2,3	0,2	1,5
50	1	3	40	4,2	1	0,4	1,5
70	1	3	40	4,2	0,43	0,4	1,5
50	1	3	40	4,2	1	1	1,5
50	1	3	40	4,2	1	0,65	1,5
50	1	2,5	40	2,9	1	0,4	1,5
50	1	2,5	40	2,9	1	0,2	1,5
30	1	2,5	40	2,9	2,3	0,4	1,5
30	1	2,5	40	2,9	2,3	0,2	1,5
50	1	2,5	40	2,9	1	0,65	1,5
50	1	2,5	40	2,9	1	0,1	1,5
50	1	2,5	40	2,9	1	0	1,5
0	0	0	40	0	1	0,4	1,5

The free phenol and formaldehyde level of the wood resins was determined. Typical residual formaldehyde levels were <0.1 w-% and residual phenol <2 w-%.

The performance window of the resins was evaluated in laboratory scale in the 'Automated bonding evaluation system' (Abes). The testing evaluated the speed of strength development of the adhesive bond under a broad range of controlled chemical, thermal and stress conditions.

As an example, testing results are plotted as function of curing time for resins cooked with 0.2 equivalents of NaOH (Figure 39).

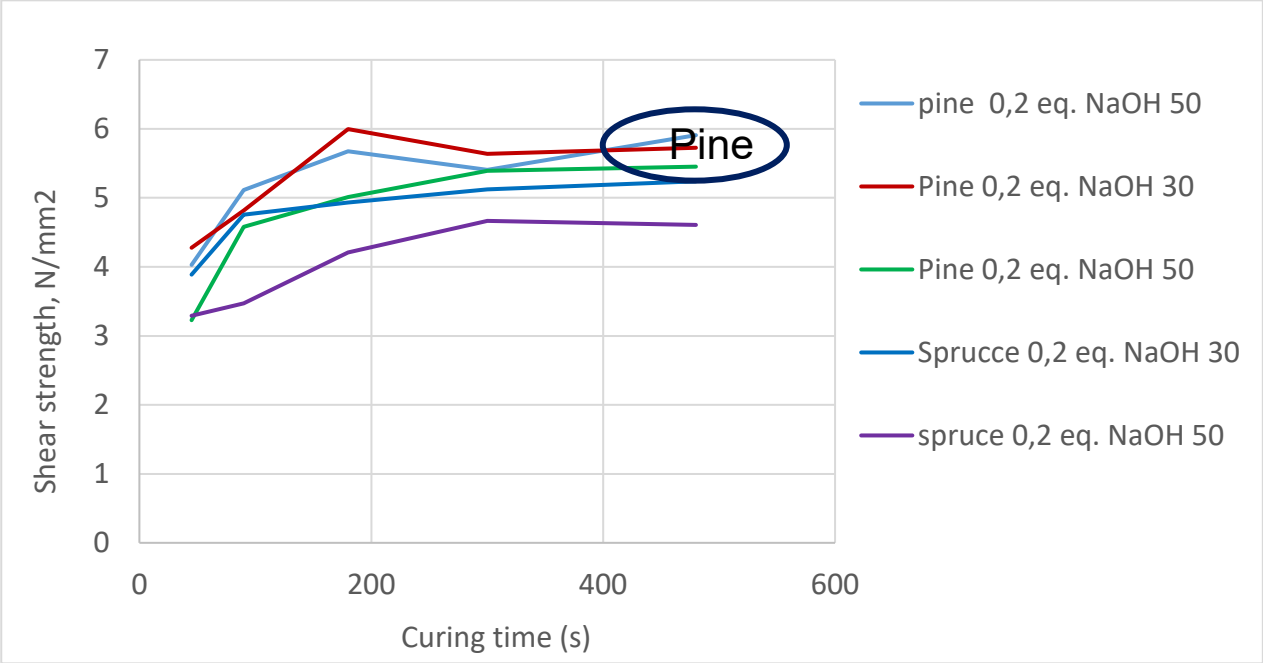


Figure 39. Abes testing results for resins with 30 and 50 % replacement of phenol with spruce and pine crude tannin at 0.2% NaOH dosage.

The shear strength level reached 4.5-6 N/mm^2 for all samples and the maximum shear strength was reached at 300-480 s for most of the trial points. At 0.2 eq. of NaOH, the resins from crude pine tannin seemed to have a higher shear strength than spruce. However, the differences between a replacement level of 30 and 50% were small for the samples from crude pine tannin.

Some of these experiments were part of a Design of Experiments (DoE) as shown in Table 13. The purpose of DoE was to determine the effect of several parameters on the shear strength of the synthesized tannin-phenol resins.

Table 13. Parameters for DoE with corresponding levels.

Parameter	Low ($^{-1}$)	High ($^{+1}$)
Tannin content	30	50
NaOHh eq. (n/pr)	0,2	0,4
Curing time	300	480
Type	Spruce	Pine

The DoE showed that tannin content had the greatest influence on the shear strength, followed by type and time. The NaOH/phenol eq. did not seem to have significant effect on the shear strength. The resin with the greatest prospects, according to DoE and ABES results, are resins containing 30% crude pine tannin.

The best recipe with crude pine tannin without and with hardener was compared to commercial resin with hardener (Figure 40) at curing times of 300s and 480 s. The experimental resin (30% crude pine tannin, 0.4 eq NaOH) displayed comparable results to commercial PF resin in ABES measurements. The achieved shear strength of tannin resin was 6.1 N/mm^2 without and 7.7 N/mm2 with 5 w-% commercial hardener at 8 min curing time.

Figure 40. Shear strength in ABES testing of experimental resin from pine crude tannin at 30% phenol replacement vs commercial resin.

The resins with replacement level of 30-50% showed thus preliminarily promising results in agreement with earlier results (D1.2 report).

Task 4.2 Tannin-hot-melt adhesives for packaging (VTT)

The objectives in this task was to develop HMA formulations with tannin as tackifier for the gluing of cardboard. The details were reported as diploma thesis (Halkosaari 2019), listed also as delivery report D4.2 in Table 23.

The studied non-reactive HMAs form adhesive bonds after melting, adhesion and cooling without chemical reaction (thermoplastic materials). HMAs are typically composed of a cohesive polymer, a tackifier (resin), diluents and waxes. The cohesive polymer has usually high molecular weight (MW) and a glass transition temperature (Tg) below room temperature. The resin in term has a low MW (<5000) and a Tg usually above room temperature. Diluent and waxes are amorphous, low MW compounds with Tg below room temperature for polymer dilution and rheology control. Tannin as replacement for tackifying resins in HMAs was selected because tannin has a suitable molar mass range and phenolic hydroxyl group functionalities favored in tackifiers. In addition, recent work has shown that lignin as another phenolic compound has potential as tackifier in HMAs (Laine et al., 2019).

Different polymers and plasticizer were screened together with crude spruce and pine tannin (MF-S-M and MF-P-M) produced by VTT in 2017 (WP1. Selection of the raw materials and preparation of the first tannin batch) for formulating HMAs in the beginning (Figure 41). Cardboard was selected as main substrate for the adhesive testing. 180° peel tests were performed after equilibration of the samples in standard conditions.

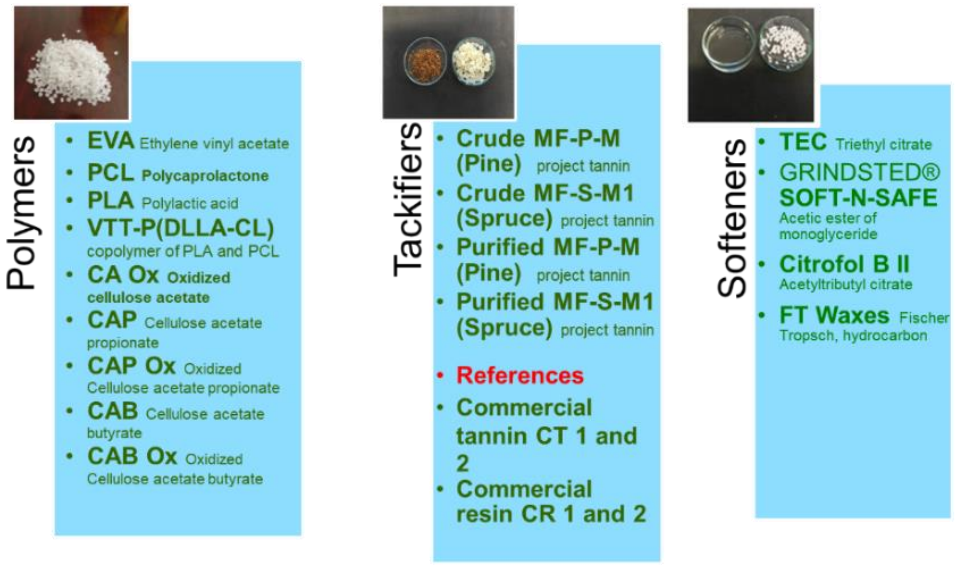


Figure 41. Compounds tested for HMA formulations.

The most promising results were obtained for a mixture of racemic lactic acid-based copolymer (P(DLLA-CL)) with crude spruce tannin and the study concentrated on this binary mixture. Lactic acid-based copolymers are attractive as cohesive polymers due to their biodegradability. The tested P(DLLA-CL) was rather soft and had a M_w of 4 440 mol/g. The polymer was tacky as such and could be processed to an HMA with tannins even without a plasticizer. It was possible to process the mixture while P(DLLA-CA) alone was too tacky. Good processability is essential for an HMA.

As an example, some formulations are shown in Figure 42. The formulation with P(DLLA-CL) and tannin at a ratio of 70:30 showed reasonable peel strength and processability at 135-140°C. An important observation was that the copolymer as such is not stable at the temperature experienced during the working period of summer 2019 in which the temperature of the laboratory was close to 30°C for several weeks. Aging decreased the strengths of the adhesive. Stabilization of the formulations is necessary also for storage at room temperature.

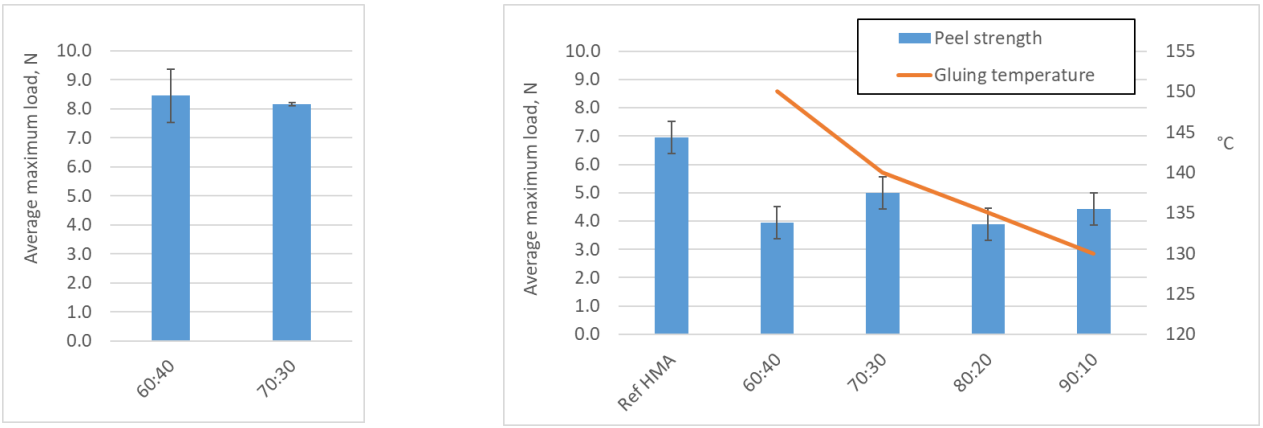


Figure 42. Peel strengths of HMA formulations P(DLLA-CL) and crude spruce tannin MF-S-M1 in different mass ratios. The temperature at which the HMA was processable is shown. Left: HMAs from P(DLLA-CL) stored in the freezer. Right: HMAs from P(DLLA-CL) stored several weeks at room temperature. Coated-uncoated.

The water resistance of the P(DLLA-CL)-tannin HMA was measured to evaluate the stability (Figure 43). P(DLLA-CL)-degradation has been reported in the literature to be caused by hydrolysis of the ester group. Therefore, the stability of the HMA against water is of special interest.

Only a small difference was observed in the peel strengths of soaked specimens. Even though P(DLLA-CL) was not protected against hydrolysis, the HMA showed decent water resistance.

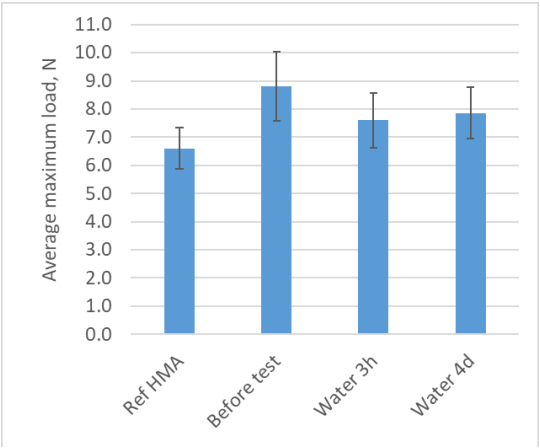


Figure 43. Peel strengths after soaking the specimens in room temperature water for the formulation of P(DLLA-CL)-tannin in the ratio 70:30. The results for the reference HMA and the developed HMA without the treatment are included. Coated-uncoated.

The formulation of P(DLLA-CL) and crude spruce tannin in the ratio 70:30 was compared to formulations with P(DLLA-CL) and other project tannins, reference tannins and reference resins.

Formulation with the following eight different tackifiers were produced:

- Crude Spruce Tannin (CST = MF-S-M1)
- Crude Pine Tannin (CPT = MF-P-M)

- Purified Spruce Tannin (PPT) see Chapter 3.1
- Purified Pine Tannin (PST), see Chapter 3.1
- Commercial Tannin 1 (CT1)
- Commercial Tannin 2 (CT2)
- Commercial Resin 1 (CR1)
- Commercial Resin 2 (CR2)

Drops of some of the produced HMAs are shown in Figure 44. On the very left is pure P(DLLA-CL), which is clear. The second from the left is the light grey mixture of P(DLLA-CL) with CR2. This mixtures with commercial resins had the advantage of being easier to spread than any mixture with tannin. The middle HMA presents the mixture of P(DLLA-CL) with CT1 and the next is the P(DLLA-CL) with crude spruce tannin HMA. Both of these seem dark brown, even black in the pictures. In reality, CT1 gave the compound a reddish brown color while P(DLLA-CL) with crude spruce tannin is indeed dark brown. The HMA on the very right is the reference HMA. As can be seen, all other HMA formulations formed droplets but REF started to solidify faster than others which led to it leaving thin filaments and therefore also no round droplet was formed.

Figure 44. Examples of HMA appearance. From left to right: Pure P(DLLA-CL), P(DLLA-CL) + CR2, P(DLLA-CL) + CT1, P(DLLA-CL) + CST, REF.

Testing results for adhesive bonds between coated and uncoated cardboard are shown in (Figure 45). The results for the reference HMA and pure P(DLLA-CL) from earlier testing were included for reference.

From the results it is evident that tannins are more compatible with P(DLLA-CL) than the commercial resins. The peel strengths of all formulations with tannins are relatively close to each other. The purified project tannins achieved similar properties, especially maximum load per weight, as crude tannins. As such purifying tannins for this formulation was not beneficial and may be omitted.

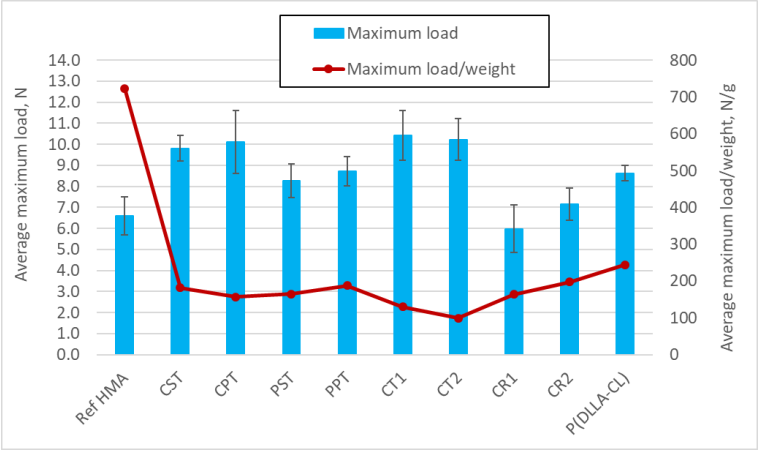


Figure 45. Peel strengths of HMA bonds between coated and uncoated cardboard for HMAs with P(DLLA-CL) and different tackifiers in the ratio 70:30. The results for the reference HMA and pure P(DLLA-CL) are included.

There was also quite strong differences in how well the mixtures could be blended. Commercial resins had an advantage over tannins by forming a homogenous mixture with P(DLLA-CL). As a consequence, the spreading of these HMAs was easier. In contrast to that, commercial tannins did not form a homogenous mixture; especially the HMA with P(DLLA-CL)-CT2 looked more like a heterogeneous dispersion. This heterogeneity lead to difficulties in spreading the adhesive which in turn lead to increased mass and thus lower strength per mass.

The viscosity for selected HMA formulations measured with a cone and plate viscometer is shown in Table 14. The viscosity range of 3.9–4.3 g cm^{-1} s^{-1} for the developed HMA formulations was comparable to the reference HMA and the reported viscosity of starch-based HMA reported earlier by VTT. HMA with purified transglycosylated starch acetate and TEC measured viscosity range of 3.2–5.2 g cm-1 s-1 (PCT/FI2003/000796). The reference HMA was quite uniform, as expected, and also very viscous. The copolymer as such was quite fluid and the viscosity increased rapidly when adding other materials. In total, the achieved viscosity range was rather narrow and the observed changes in viscosity during accelerated aging at elevated temperatures were small. This is an interesting result because the formulated HMAs did not contain any stabilizers or other additives and should rather be described as HMA prototypes.

Table 14. Measured viscosity for HMA formulations with a cone and plate viscosimeter.

Hma formulation	Viscosity (g cm^{-1} s^{-1} (poise))
Ref hma	6,2 ± 0,1
P(dlla-cl) + crude spruce tannin	3,9 ± 0,6
P(dlla-cl) + crude spruce tannin, aged 24 h at 60 °c	4,3 ± 1,4
P(dlla-cl) + crude spruce tannin, aged 24 h at 140 °c	3,3 ± 0,6
P(dlla-cl) + commercial tannin ct1	Did not melt homogeneously
P(dlla-cl) + commercial resin cr2	4,3 ± 1,8
Pure p(dlla-cl)	1,7 ± 0,3

It is concluded, that a mixture of tannins and poly(DL-lactide-co-ε-caprolactone) is a potential hot melt adhesive. The copolymer can be used as a hot melt adhesive by itself, but the processability and adhesion towards uncoated boxboard increased with tannins. In future research, the mixing should be developed as the tannin-copolymer mixture was not fully homogenous. There should also be research into how the parameters of the copolymer affect the adhesive capabilities of the hot melt adhesive.

Milestones and deliverables

- **MS 4.3** Partially purified tannin evaluated as wood resin (month 24)
- **MS 4.4** Partially purified tannin evaluated as hot-melt adhesive (month 24)

- **D 4.1** Tannin-wood-adhesives for particleboard, plywood and MDF (month 28)
  Reported as Bachelor thesis (Berghuis, 2018)
- **D 4.2** Tannin-hot-melt adhesives for packaging (month 28)
  Reported as Master Thesis (Halkosaari, 2019)

6. WP5. Applications and testing

Task 5.1 Tannin-wood-adhesives for plywood (Xamk)

Aim of this task was to test experimental tannin-phenol resins for a small scale plywood manufacturing and compare the result to commercial references. There were three experimental tannin-resin and two commercial resins. This study was done at Xamk.

The actions included:

- Preparation of the test materials and glues
- Manufacturing of the tests product
- Cutting, conditioning and preparation of the test specimens
- Mechanical tests using standard industrial tests and procedures

Preparation of the veneers

This study started by sizing and grading the veneers to a suitable form for the pilot plywood manufacturing. The final size of the veneers was determined by Xamk wood laboratory's small scale hot press (Figure 46). The veneers were birch with the thickness of 1.5 mm. The veneers were manufactured by a commercial plywood manufacturing line.

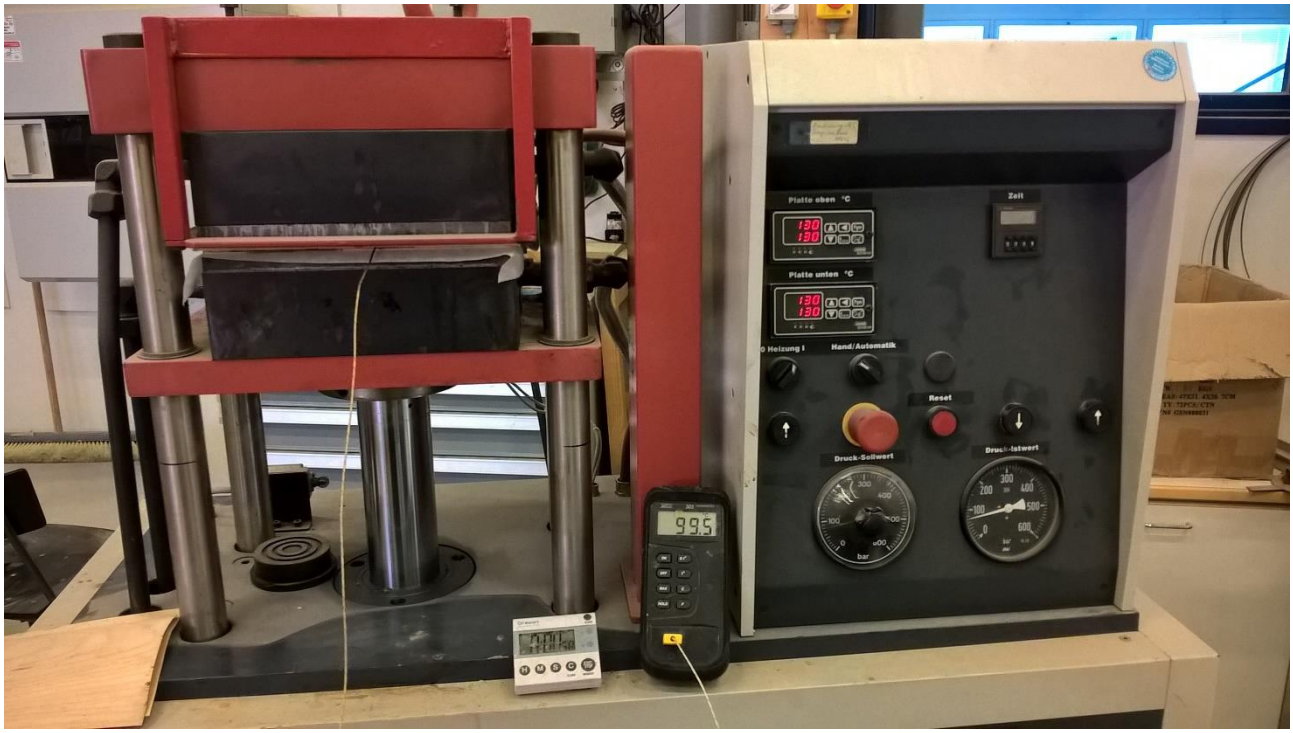


Figure 46. Hydraulic press. The plate size 250 mm x 250 mm (Xamk-Wood laboratory).

The glue mixtures

Three experimental tannin resins (Table 15), Hexion and Prefere Resin references including hardeners were sent to XAMK 11.6.2018 by VTT for plywood gluing tests.

Table 15 The experimental tannin resins prepared at VTT used in adhesive tests

ID	Source of tannin	50-50 (tannin-phenol)	Total NaOH w% in cooking	pH at end of cooking
AB.2.69 (=AB2.85)	pine	0,65 eq (NaOH / phenol)	5,3	9,9
AB.2.83 (=AB2.41)	pine	0,2 eq (NaOH / phenol)	2,9	8,7
AB.2.87	spruce	0,65 eq (NaOH / phenol)	5,1	10,0

The mixing tests was started with Prefere commercial resin. Prefere mixture was prepared with the manufacturer's recipe (e.g. 1000 g resin, 240 g hardener and 310 g water). Mixing of the experimental tannin-phenol resin was done with Hexion PFH 6030 hardener and the target amount was according to the ABES results (addition of 5 %). The viscosity of the mixtures were adjusted with the amount of water so that the viscosity is more or less the same than Hexion resin (Table 16). The target formulation for Hexion resin was 70 % resin; 14 % hardener and 16 % water. The mixtures of test adhesives were made in plastic box using manual stirring. Viscosity measurements were done by using the ford cup 4.

Table 16 Mixing ratios (resin, hardener and water) and viscosity

ID	Resin (g)	Hardener (g)	Water (g)	Total (g)	Viscosity (s)
Prefere reference (P)	154,80	37,20	48,00	240,00	115
AB.2.69 (MA)	200,00	10,00	13,08	223,08	80
AB.2.83 (MB)	189,00	10,02	30,38	229,40	84
AB.2.87 (K)	206,04	10,14	15,08	231,26	80
Hexion reference (H)	216,24	44,30	50,00	310,54	80

The plywood pilot manufacturing

The glue was applied by hand using the rubber roller (Figure 47). All the test panels were laid up into 5 ply plywood. The glue was applied on one side of the veneer; the glue also transfers to the uncoated side of the veneer when applying the next layer. The average amount of the glue was 128 g/m². After the last glue application, the panel was moved directly to the hot press.

Figure 47 Glue application by hand (rubber roller)

In this preliminary pilot scale tests the pressing parameters were selected as close as possible to the normal birch plywood proses (pressure and temperature). The curing time and the temperature were determined in the middle of the first test panel. The total amount of the manufactured test panels were five for the each adhesive.

Pressing parameter for all test panels (Figure 48):

- Temperature 130 °C (hot plates temp),
- Pressure 1,8 Mpa and
- Pressing time 420 s.

Figure 48 Test panels (5 ply; 250 mm x 250 mm)

EN 314-1 Mechanical test

The plywood test panels were trimmed before cutting the test pieces conforming EN 314. The test pieces was prepared according to EN 314-1 standard. The total amount of the test pieces was 30 for every test adhesive. One set of test pieces is shown in Figure 49. All test pieces were immersed in water for 24 h before the shear tests.

Figure 49 EN 314-1 test pieces

The shear test was carried out on wet test pieces. The shear test area was 25 mm x 25 mm. The test frame was MTS systems manufactured testing device. The results of shear test are in Table 17.

Table 17 Shear test results

Shear strength (n/mm²)					
Glue	**Prefere (ref.)**	**Hexion (ref.)**	**AB.2.69 (MA)**	**AB.2.83 (MB)**	**AB.2.87 (K)**
Average	1,77	1,69	0,25	0,41	0,29
Maximum	2,58	2,31	0,47	0,68	0,38
Minimum	0,98	1,07	0,11	0,16	0,24
St. Deviation	0,41	0,37	0,10	0,14	0,05

The strengths of the experimental tannin-resins were significantly lower and decomposed from the glue-line (Table 17). The commercial resin test result are from 30 test pieces, but most of the experimental tannin-resin test pieces were split up before the shear test.

All failures in the commercial resin occurs in the wood or in the glue-lines (Figure 50), but all experimental tannin-resin failures occurred in glue-lines (Figure 51).

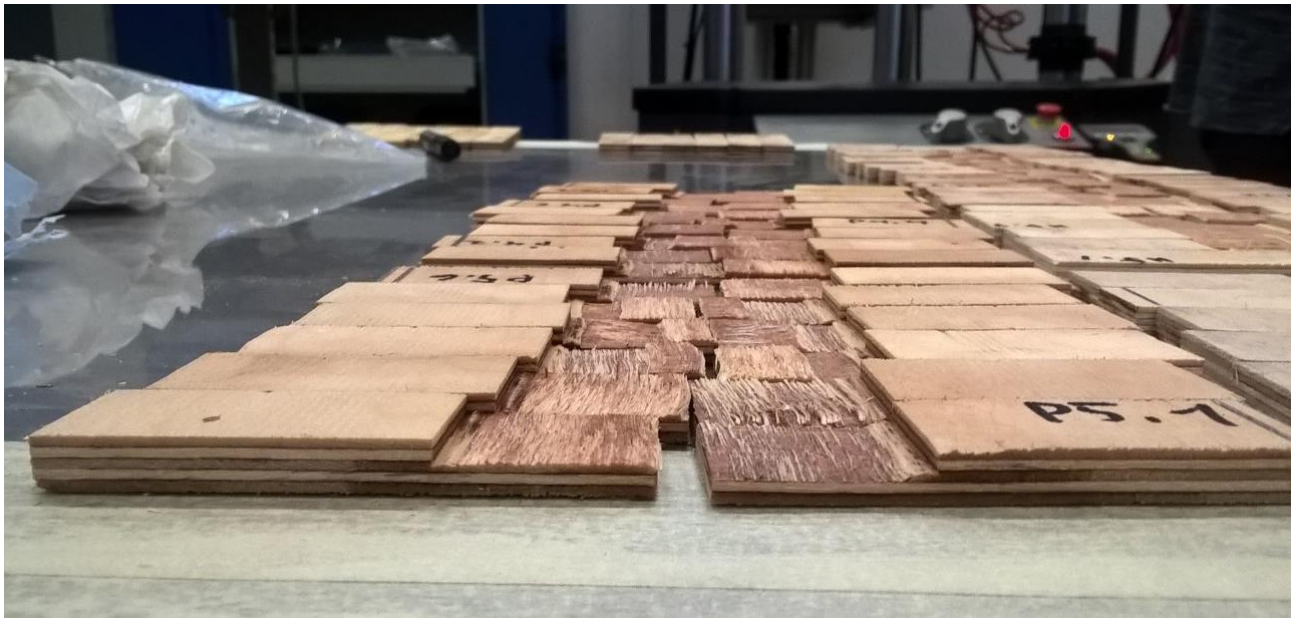


Figure 50 Commercial resin after water immersion and shear test

Figure 51 Experimental tannin-resin after water immersion and shear test

Discussion and conclusion

There were only a small difference between the adhesives during the glue mixing. One difference was seen the color of the mixtures. Commercial resin were slightly darker than experimental resins. The highest difference between the adhesives was in their viscosity. The viscosity of experimental tannin-resins were lower than commercial resins. This also affected the final amount of water in the mixtures. How this effect on gluing? In this study, the target amount of hardener in experimental tannin-resins was 5 % and the viscosity was adjusted in line with Hexion commercial resin mixture. The viscosity measurements based on

the measuring cup (ford cup 4). Optimization of the resin mixtures might need further testing with ABES, for instance testing with larger ratio of hardener and water in the mix could be interesting.

All test boards were manufactured with similar process parameters. The shear test results show that the strengths of the experimental tannin-resins were significantly lower and the failures were in glue-line. When looking at cohesive of wood failure, it seems that the glue has dried too quickly and/or glue penetration was not good enough. The small test panel size may have some effect. The moisture and glue movements during the hot pressing might be different, when compared a small test panels versus large test panels (edge effects). But all three experimental resin syntheses practically degraded by 24 h water immersion, so it looks like the water immersion before the shear test have a high effect on this test results. As the water immersion is quite severe pre-treatment, one option in further test series would be to conduct the mechanical testing with "dry" (humidity controlled) specimens. This could provide more useful insights about the failure process. Moisture behavior is obviously an important characteristic too.

New possibilities improving the following test series

Xamk wood laboratory has a new modified hot press available for use. The hot plates size is 1300 mm x 850 mm, which means that it is possible to do larger test panels (Plywood, LVL etc.).

Resins test (Xamk)

Aim of this task was test a new batch of experimental tannin-phenol resins for small scale plywood manufacturing and compare the result to commercial references. There were two experimental tannin-resin and same commercial resins as in the first study. This study was performed also at Xamk Mikkeli in Materials technology laboratory. In this test series the specimens were not immersed in water prior to measurement.

The test with wood resins included:

- Preparation of the test materials and glues
- Manufacturing of the tests product
- Cutting, conditioning and preparation of the test specimens
- Mechanical tests using standard industrial tests and procedures

Preparation of the veneers

This study was started by sizing and grading the veneers to a suitable form for the pilot plywood manufacturing. The final size of the veneers was determined by Xamk wood laboratory's small-scale hot press (Figure 52). The veneers were birch with the thickness of 1.5 mm. The veneers were manufactured by commercial plywood manufacturing line.

Figure 52 Polystat s 200. The plate size 250 mm x 250 mm (Xamk Wood Laboratory)

The glue mixtures

Experimental resins used in adhesive tests are presented in Table 18.

Table 18 The experimental tannin resins prepared at VTT used in adhesive tests

ID		Raw material	Tannin/ phenol ratio	NaOH/ phenol, eq	Viscosity^, poise	Residual formaldehyde, %	Residual phenol, %
2019_1	Experimental 1	Crude spruce tannin#	50/50	0.65	3.3	< 0.05	1.76
2019_2	Experimental 2	Purified spruce tannin*	50/50	0.65	3.0	< 0.05	2.20

With both tested resins, 50% of phenols was substituted with tannin. With Experimental 1 substitution was done with crude spruce tannin and with Experimental 2, the substitution was done with spruce tannin from which carbohydrates were removed.

The resins were stored in freezing conditions until mixing. The mixing tests were started with Prefere commercial resin. Prefere mixture was prepared with the manufacturer's recipe (e.g. 1000 g resin, 240 g hardener and 310 g water). Mixing of the experimental tannin-phenol resin was done with Hexion PFH 6030 hardener and the target amount was according to the ABES results (addition of 5 %). The viscosity

of the mixtures were adjusted with the amount of water so that the viscosity is more or less the same than Hexion resin (Table 19). The target formulation for Hexion resin was 70 % resin; 14 % hardener and 16 % water. The mixtures of test adhesives were made in plastic box using manual stirring. Viscosity measurements were done by using the ford cup 4.

Table 19 Mixing ratios (resin, hardener and water) and viscosity

ID	Resin (g)	Hardener (g)	Water (g)	Total (g)	Viscosity (s)
Hexion ref.	210,3	40,8	48,9	300	65
Prefere ref.	193,5	46,5	60	300	180
Experimental 1	237,5	13,4	47,51	298,41	60
Experimental 2	237,7	12,55	52,42	302,67	51

Experimental resins 1 and 2 viscosity was measured also without hardener and water. Experimental 1 viscosity was little bit higher than experimental 2. The viscosity was 220 seconds for the experimental 1 and 195 seconds for the experimental 2 resin (temperature 20 °C).

The plywood pilot manufacturing

The glue was applied by hand using the plastic ruler (Figure 53). All the test panels were laid up into 5 ply plywood. The glue was applied on one side of the veneer; the glue also transfers to the uncoated side of the veneer when applying the next layer. The average amount of the glue was 193 g/m². After the last glue application, the panel was moved directly to the press. A few panels were tested with pre-pressing before hot press.

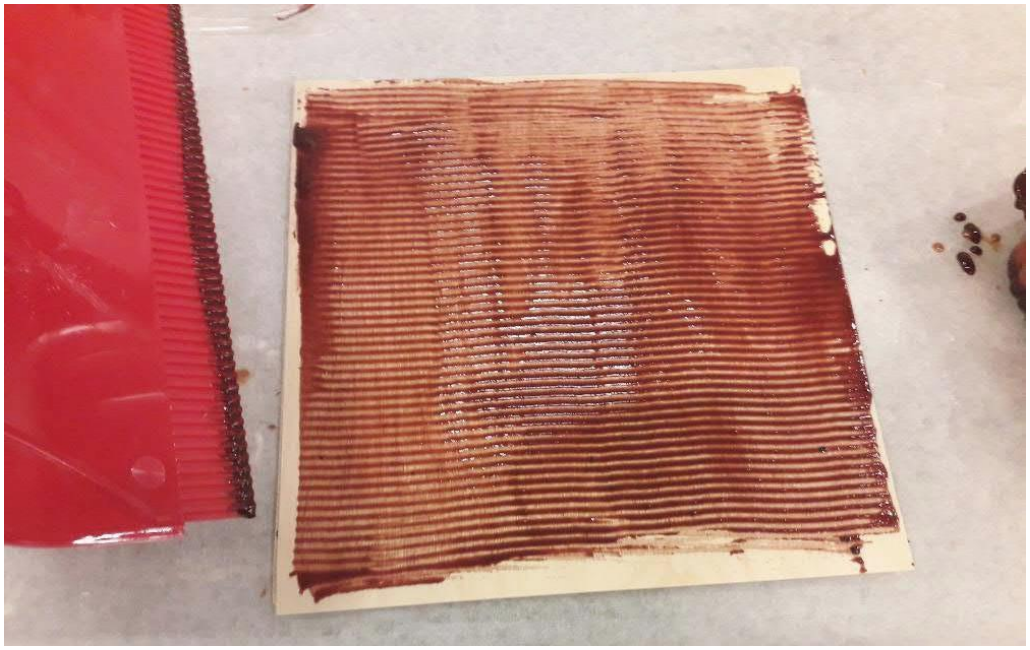


Figure 53 Glue application by hand (plastic ruler).

In this preliminary pilot scale tests the pressing parameters were modified in the last study. The parameters selected as close as possible to the normal birch plywood proses, but temperature was slightly higher. The curing time and the temperature were determined in the middle of the first test

panel. The total amount of the manufactured test panels were five for the both experimental resins and tree for the commercial resins.

Pressing parameter for all test panels (*Figure 54*):

- Temperature 150 °C (hot plates temp),
- Pressure 1,8 Mpa and
- Pressing time 480 - 510 s.

Figure 54 Test panels (5 ply; 250 mm x250 mm)

EN 314-1 Mechanical test

The plywood test panels were trimmed before cutting the test pieces conforming EN 314. The test pieces were prepared according to EN 314-1 standard. Four test pieces were sawn from one test panel and two of them were tested dry. The total amount of the test pieces was 20 for both experimental test.

Table 20 Shear test results

Shear strength (n/mm²)				
Glue	**Prefere (ref)**	**Hexion (ref)**	**Experimental 1**	**Experimental 2**
Average	2,67	2,10	1,52	**1,25**
Maximum	3,39	2,65	2,02	**1,80**
Minimum	2,08	1,60	1,10	**0,80**
St. Deviation	**0,40**	**0,36**	**0,34**	**0,30**

The strengths of the experimental tannin-resins were slightly lower than commercial resins (Table 20). All failures in the commercial resin occurred in the wood or in the glue-lines, but all experimental tannin-resin failures occurred in glue-lines. Figure 55 shows examples of wood failure and shows the difference between the commercial and experimental resins.

Figure 55 Test specimens after shear test

Discussion and conclusion

In this study, there were only a small difference between the adhesives during the glue mixing. One difference was noticed in the colour of the mixtures. Experimental resins 1, 2 and Prefere resin were darker brown than Hexion resin. The highest difference between the experimental resins was in their viscosity. The viscosity of the experimental resin 1 was higher than experimental resin 2 (temp. 20 °C). This has a minor effect in the final amount of water in the glue mixtures, but affects the gluing. In this study, the target amount of hardener in experimental tannin-resins was 5 % and the viscosity was adjusted in line with Hexion commercial resin mixture. The viscosity measurements based on the measuring cup (ford cup 4).

The test specimens were tested without water immersion, so the shear strengths were better compared to the first study in which the specimens were tested after water immersion. When looking at cohesive of wood failure, it seems that the experimental resins were still broken from the adhesive joint. Either the resin dries too quickly and at the same time the resin does not penetrate the veneer sufficiently or the penetration is sufficient but the resin seal is too weak. In this study, the effect of pre-pressing was also

tested, but this did not have effect on final results of this study. Optimization of the resin mixtures might need further testing with ABES, for instance testing with larger ratio of hardener and water in the mix could be interesting. It would be good to find some limit values for these experimental adhesives (resins-hardener-water). It would be also interesting to try pre-pressing and hot press with different amounts of glue and see how this effect on glue joints and shear strengths.

Task 5.2 Hot melt Glues (Xamk)

Preliminary tests with VTT provided hot-melt adhesive were performed at Xamk Mikkeli in Materials technology laboratory.

Manufacturing of the tests plywood

Steps for plywood pilot manufacturing:

- Ready-made veneer sheet from the factory (Hardwood).
- Cutting the veneer sheets (250 mm x 250 mm)
- Melting the glue (+90 °C)
- Glue application
    - Estimated amount of glue 128 - 200 g/m2
    - 5 Ply plywood
- Plywood pressing
    - Pressing parameters 150 °C / 1.8 Mpa
    - Hydraulic press: Polystat 200 S (heating plates 250x250mm)

Preparation of the test materials

The hot-melt adhesive from VTT is shown in Figure 56.

Figure 56 Hot-melt adhesives from VTT

Because the dark brownish color of the adhesive it was decided that instead of original aim to test hot-melt adhesive with carton the test was performed with veneer sheets. Application of the glue was done by hand (Figure 57).

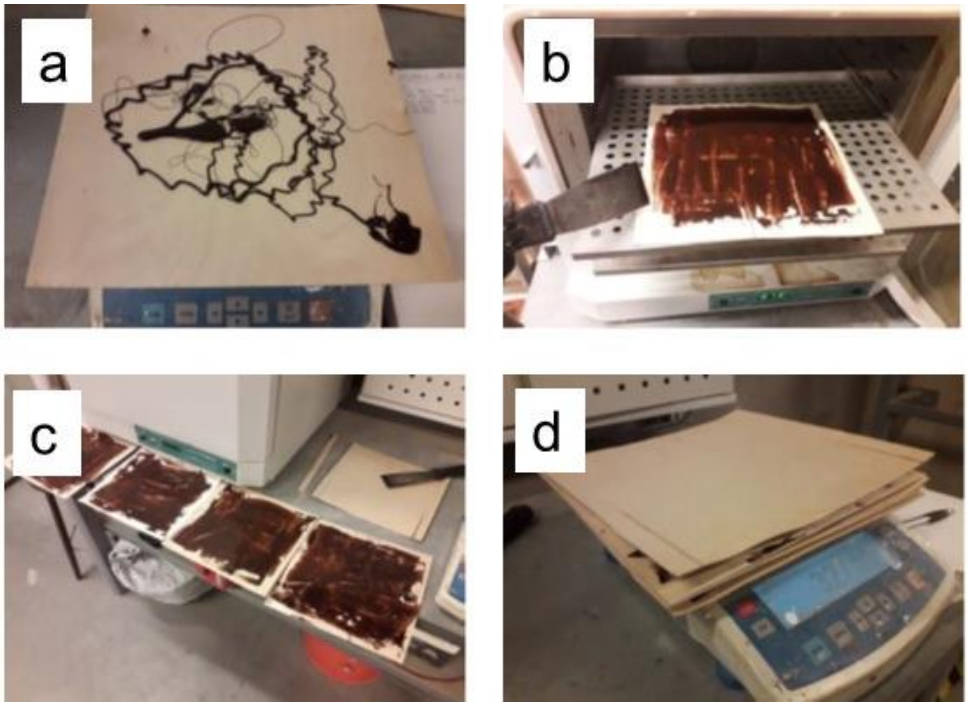


Figure 57 Application of glue and veneer layup a) dosing the glue (128-200 g/m^2) b-c) application by hand d) veneer layup /5 ply.

Manufacturing of the tests plywood

Samples were pressed with Polystat s 200 hot-press.

The pressing parameters:

- Polystat S 200 plates temperature 150 °C
- Pressure 1.8 Mpa
- Time 600 s. + cooling down under the pressure.

Test result can be seen in Figure 58. The adhesion was minimal so this hot-met glue used with veneer was not working. Further testing is needed but within this project, no more hot-melt glue was available.

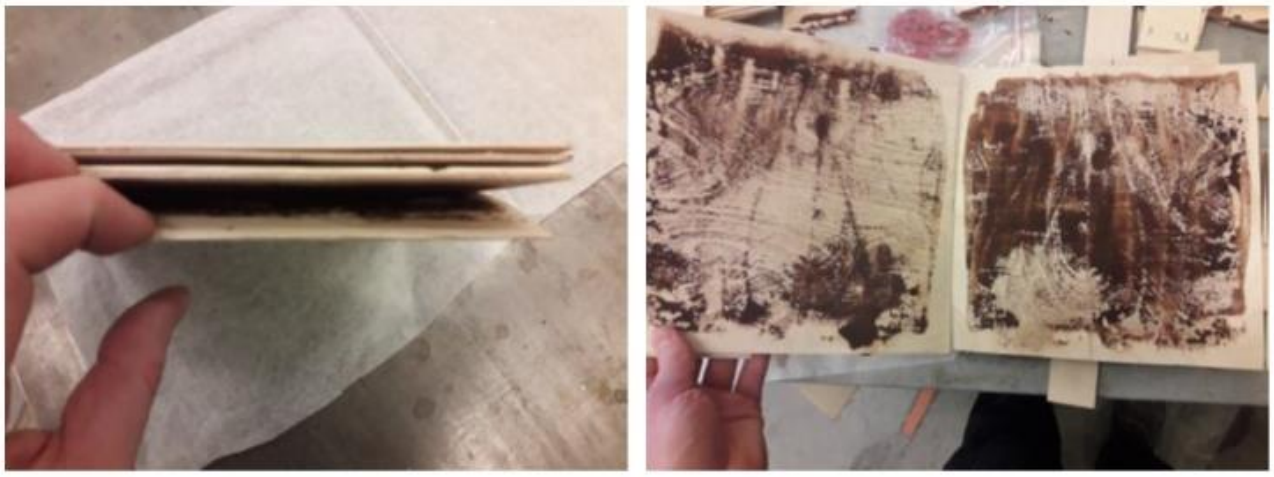


Figure 58 Hot-melt test results

Milestones and deliverables

- **MS 5.1** Wood product prototypes (plywood, CLT, and performance tests by using wood bark tannin binders by WP's 3 and 4 (month 18).
- **MS 5.2** Tannin holt-melt binder tests for lap shear, peel, detaching and heat stability (month 24).

- **D 5.1** Application and performance tests for tannin-wood-adhesives for particleboard, plywood and MDF (months 30) 31.5.2020
- **D 5.2** Applications and performance tests using formulated tannin-hot-melt adhesives for packaging (month 30) 31.5.2020

7. WP6. Techno-economic evaluation

Task 6.1 Techno-economic evaluation (VTT, Luke, Xamk)

The tannin extract was aimed to replace phenol in wood resins used for plywood or laminates, or to be used as a tackifier component in the hot melt adhesives (HMAs). In case of wood resins, tannin extract would replace 30-50 % of phenol in the resin. Current phenol price is approximately 1 €/kg (Straathof & Bampouli). In case of HMAs, tannin would replace a tackifier, either as a component in commercial fossil-originated hot melt adhesive or as a biobased tackifier component in a completely bio-originated hot melt adhesive. The glueing tests showed that tannin extract can replace tackifier completely. The current price of fossil-origin HMA is approximately 3.5-4.0 €/kg and bio-based HMA approximately 4.0-4.5 €/kg (Metsä Board). Based on typical composition of HMA, a cohesive polymer 20-25 %, tackifier 25-30 %, and diluents and waxes 40-50 %, tackifier price was estimated to be approximately 3 - 7 €/kg.

Techno-economic assessment (TEA) was divided to two parts

1. Light techno-economic analysis (TEA) of several chosen process concepts, which consists of conceptual level cost estimate and is based on the current understanding of the process steps
2. More detailed design and techno-economic assessment of the selected, most promising concept

In the light techno-economic analysis the production cost of tannin extract (€/t tannin dry) was calculated for several concepts and scenarios, and the most significant cost factors were identified. Process concept options were chosen in the project work-shop, and are summarised in Figure 59. The baseline concept was the concept consisting of all possible process unit (milling, extraction, pressing, filtration enzymatic hydrolysis, membrane filtration, evaporation and spray drying). As can be seen from Figure 59, the simplest concept would be to exclude carbohydrate removal and use the tannin extract in liquid form for wood resins. That would decrease the unit operations to milling, extraction, pressing, filtration, and evaporation (5 process units).

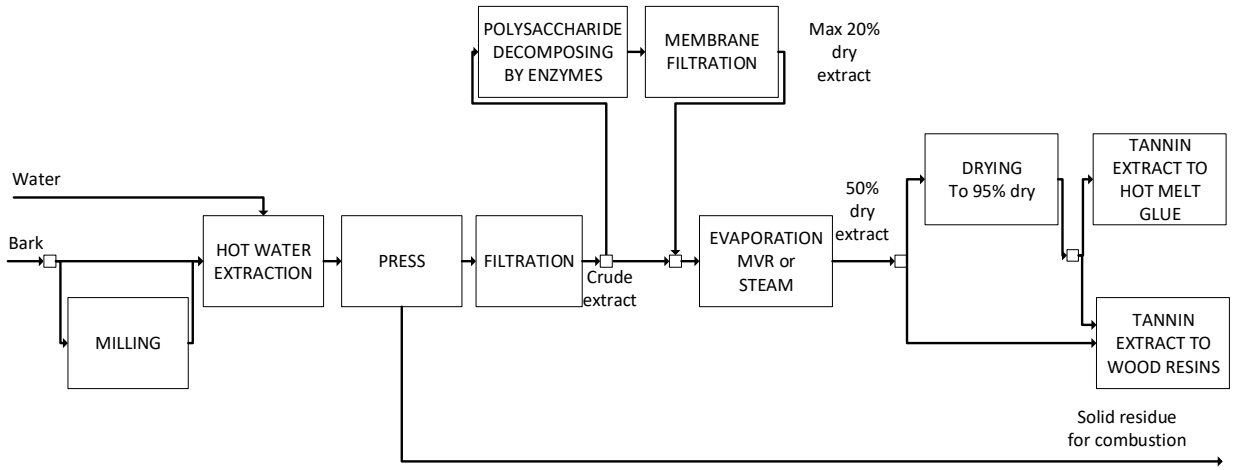


Figure 59. Process concept options.

Integration options, their benefits and drawbacks are listed in Table 21. Plant capacities were based on the integration options. The wet bark input of the extraction plants considered were 140 000 t/a (pulp mill) and 20 000 t/a (other integration options).

Table 21. Integration options (benefits and drawbacks).

	Pulp mill	Saw mill	Power plant	Plywood plant
Bark available	+ (lower quality)	+ (better quality)		+
Steam available	+		+	
Waste water treatment plant	+			
Combustor to solid residue	+?	+?	+?	
Product utilisation				+

Mass balances were calculated based on the yield in extraction measured in experimental work (14 wt% dry extract per dry bark). Overall yield (t dry tannin extract/t dry bark input) in the baseline concept was 8.7 % and in the concept with no hydrolysis 11.3 %.

The production costs are presented in Table 22. Based on the results, when replacing phenol (current price approximately 1 €/kg), only large scale scenarios without enzyme treatment were feasible. In case of using the tannin extract for replacing tackfier in HMAs, the feasibility depends on the tackifier price.

Table 22. Concept and integration option screening, resulting estimated production cost for tannin extract (€/kg dry tannin extract).

Integration option	Pulp mill	Saw mill	Power plant	Plywood plant
Scale	Large	Small	Small	Small
Evaporator type	Multiple-effect	MVR	Multiple-effect	MVR
Production cost	€/kg dry extract	€/kg dry extract	€/kg dry extract	€/kg dry extract
Process concept				
Baseline concept	2.2	3.3	3.2	3.4
Baseline concept, wet product	2.0	2.9	2.8	2.9
No hydrolysis	0.7	1.6	1.5	1.7
No hydrolysis, wet product	0.6	1.2	1.2	1.3

Production cost distribution comparing all cases is presented in Figure 60. The results showed that the operation is capital intensive, and that increasing capacity reduces the production cost significantly. The annuity of the investment cost is dominating the production costs in cases without enzymatic hydrolysis. The annual enzyme cost is significant in addition to the investment cost in the cases with enzymatic hydrolysis. Enzyme cost is directly proportional to enzyme consumption and thus if less enzyme were used, it would decrease the enzyme cost. Enzyme recycling may have positive effect to the production cost, however it is not clearly beneficial since it causes a more complicated process, higher investment costs and higher electricity consumption.

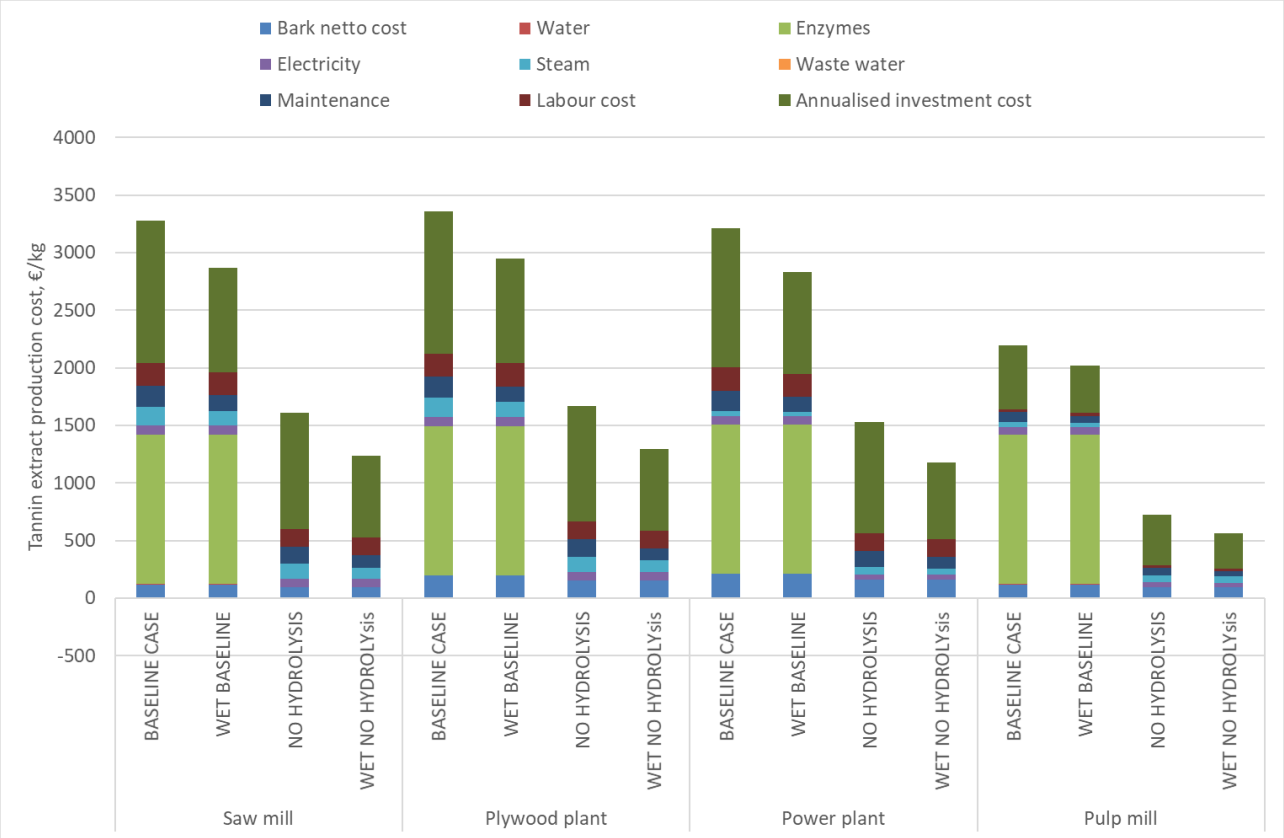


Figure 60. Production cost distribution of all cases.

The Susbinders project consortium chose one concept and one scenario for more detailed analysis based on the results of light techno-economic assessment and based on the experimental work carried out during the project. The chosen concept and the integration scenario for more detailed assessment was the large-scale straightforward solution with dried pulverised product, integrated with a pulp mill. The reasons for the choice were the significant decrease in production cost depending on scale in the light techno-economic analysis and no superior performance observed in experimental work for purified tannin compared to crude tannin in the tested applications.

At the middle size pulp mill, the annually available wet bark is around 140 000 t. Typically the dry matter content of this bark is on average 40% (56 000 t/a dry bark). The integration scenario to pulp mill provided following benefits. Bark is available at site, thus no transportation costs needs to be taken into account. There is a combustor for solid bark residue at site (again no transportation needed) and a waste water treatment plant (potential for lower waste water cost). Low-cost steam is also available, due to which the multi-effect evaporator system was chosen for the concept.

The simplified process flow sheet is presented in Figure 61. 5-effect evaporation system (5 evaporators in series) was considered economically the most feasible solution. Evaporated water was recycled for extraction, so no water addition was needed. The overall yield of dry extract from dry bark is 12.4%. Tannin extract production was 7300 t/a (DM 95%).

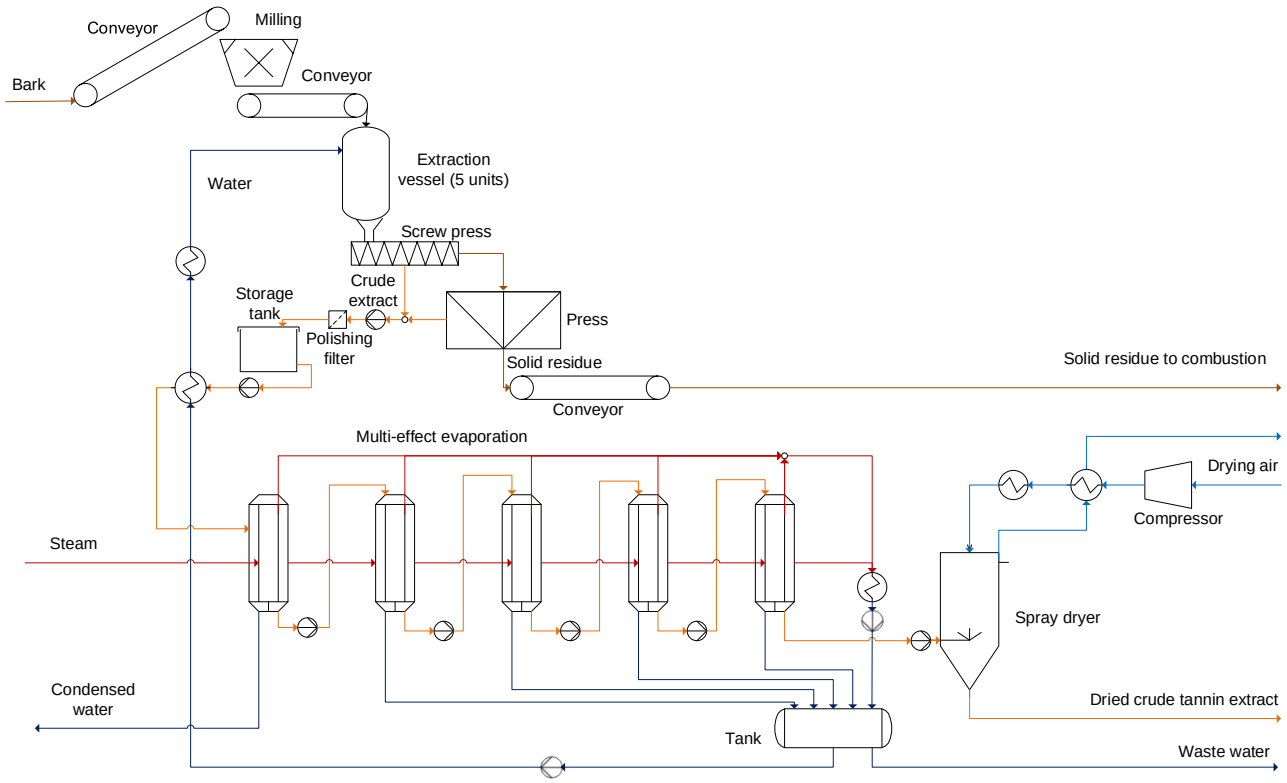


Figure 61. The simplified process flow sheet.

The calculated purchased equipment cost estimate was 10 M€. Fixed capital investment (FCI) was 28 M€, calculated based on the purchased equipment cost, using factors for direct costs, indirect costs and for contingency. The operating margin (EBITDA) was 4 M€, when assuming tannin extract price of 800 €/t. The distribution of annual costs and revenues is presented in Figure 62. Bark cost and solid residue price was 70 €/MWh, electricity cost 50 €/MWh, and steam cost 5 €/MWh.

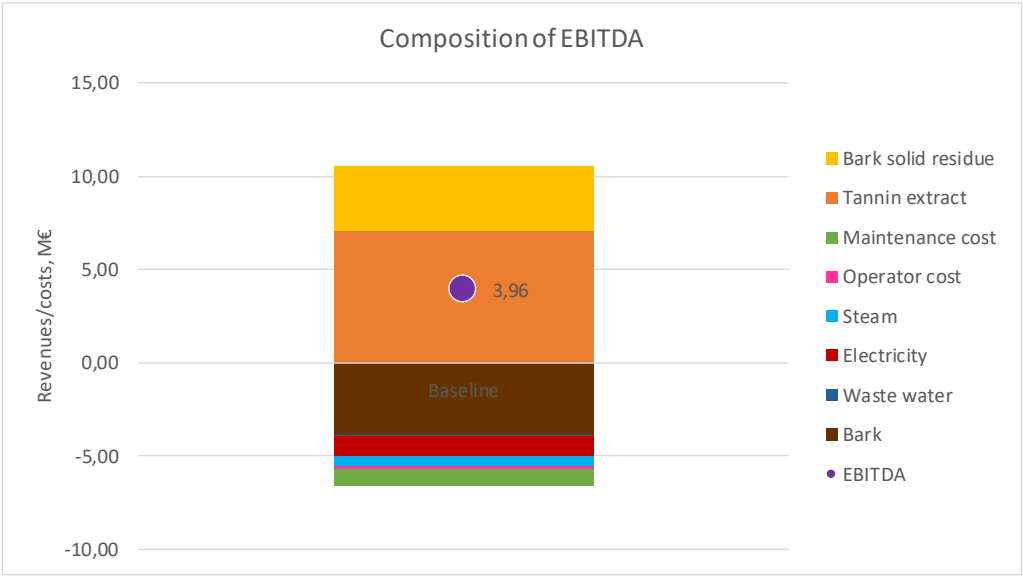


Figure 62. Cost distribution of overall profit (EBITDA). Assumed price of tannin extract 800€/t(dry).

The annual cash flow and the discounted and cumulative cash flow are presented in Figure 63, using 8% rate of return and assuming the price of tannin extract 800€/t (dry). Net present value was 0.9 M€ and internal rate of return (IRR) 8.4%.

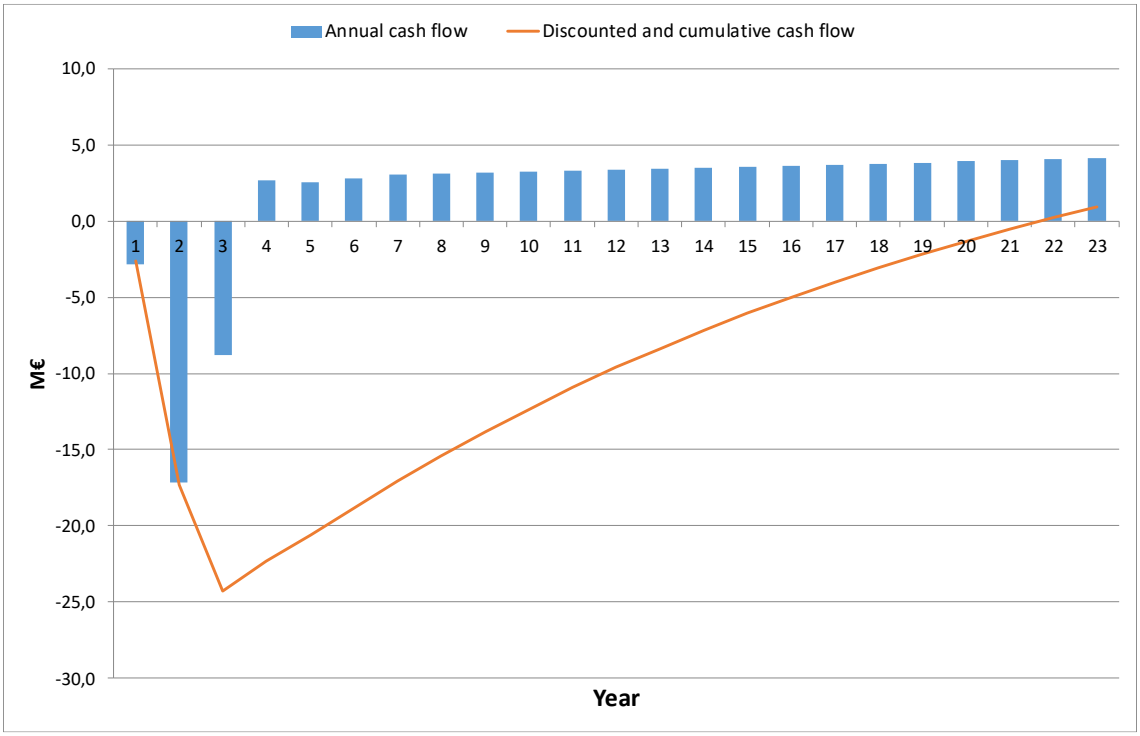


Figure 63. Annual and discounted and cumulative cash flow. (Assumed price of tannin extract 800€/t(dry))

The sensitivity analysis showed the key parameters affecting the profitability of the plant. One of the most significant parameters was the yield of dry tannin extract per dry bark during extraction. The sensitivity of IRR to the yield of dry tannin extract per dry bark during extraction is presented in Figure 64. The baseline yield used in this assessment was 14%, which is the highest experimental result obtained during this project. However, in earlier projects significantly higher yields (up to 20%) has been reported for example by Kemppainen (2015). If the extraction yield was increased from 14% to 20%, the IRR would increase from 8.4% to 13.7%. The yield is affected by several factors, including at least the freshness of the wood when barking, the wood content in the bark, the time passing between barking and milling, and drying of bark during the milling. In this project the experimental work was not totally optimized, and several days delay occurred for example between milling and extraction. Thus there may be potential for higher yield.

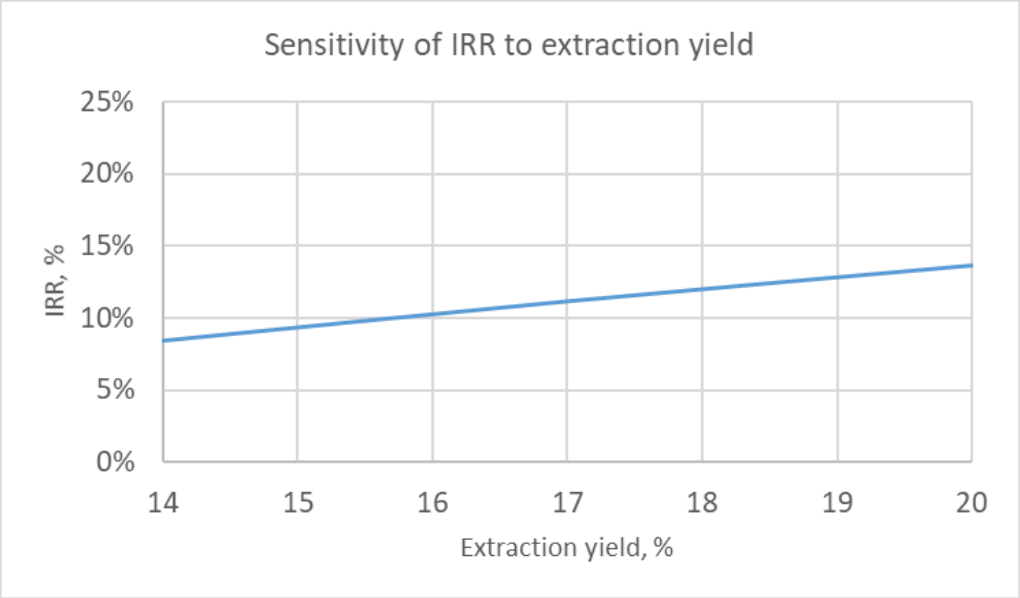


Figure 64. Sensitivity of IRR to the yield of dry tannin extract per dry bark during extraction (baseline in the assessment 14%).

The other identified key parameters having strong effect on IRR were the price of the tannin extract, fixed capital investment and steam price. The increase in tannin price from 800 €/t to 900 €/t would increase the IRR from 8.4 to 10.5%. Consequently, also the decrease in tannin price has strong effect to IRR. The accuracy of investment cost estimates based on factorial method and main equipment purchase costs is typically assumed to be around ±30%, thus the similar range was included in the sensitivity analysis. When varying the investment cost estimate from -30% to +30%, IRR varied from 5.5% to 13.4%. The integration to the pulp mill was assumed to provide low-cost steam for the plant, and the concentration method was chosen based on this assumption. Significant change in steam price would affect IRR and would require to reconsider the concentration method. Thus increase in the steam price may affect to the investment cost.

As conclusion, for replacing low-price bulk chemicals, tannin extraction process requires a large scale to be profitable. If a higher-value applications were found, also smaller scale operation could be profitable. Increasing tannin concentration by removing carbohydrates in enzyme hydrolysis would require at the current enzyme price an application in which the tannin extract price could be over 2000 €/t. Research and development work is recommended to include testing the extract material containing carbohydrates for different applications. The applications in which carbohydrate removal is not necessary, will benefit in lower production cost of extract. If the reduction of carbohydrate concentration is required, optimizing the enzymatic hydrolysis is one of the most important subjects.

Milestones and deliverables

- **MS 6.2** Light techno-economic analysis conducted and results presented to the consortium (Month 25)
- **MS 6.3** Concept selected for more detailed techno-economic analysis (Month 30)

- **D 6.1** Light techno-economic analysis and design and techno-economics of the selected concept (month 36) 14.5.2020

8. WP7. Management and dissemination

Task 7.1 Management (VTT)

Consortium meetings

- 1st Steering group meeting (21.6.2017) - kick off
- 2nd Steering group meeting (22.1.2018)
- 3rd Steering group meeting (1.6.2018)
- 4th Steering group meeting (12.10.2018)
- 5th Steering group meeting (24.5.2019)
- 6th Steering group meeting (13.12.2019)
- Final Steering group meeting (15.5.2020)

Other meetings

- Roughly biannual project partner meetings throughout the project
- Visit of VTT Group to Xamk in Autumn 2017

The project reported in biannual reports and Deliverable reports to the project consortium (Table 23).

Table 23. List of project reports.

Reports	Authors	Distributed
Biannual reports		
Biannual progress report, months 1 - 6 (1.6.2017 - 30.11.2017)	Alakurtti S, Laine C, Borisova A, Salonen P, Hohenthal C, Suomalainen M, Behm K, Kruus K, Pulkkinen L, Tirri T, Kilpeläinen P, Saranpää P	12/2017
Biannual progress report, months 7 - 12 (1.12.2017 - 31.5.2018)	Alakurtti S, Laine C, Borisova A, Suomalainen M, Berghuis A, Halkosaari V, Kruus K, Pulkkinen L, Tirri T, Kilpeläinen P, Saranpää P	5/2018
Biannual progress report, months 13 - 18 (1.6.2018 - 30.11.2018)	Alakurtti S, Laine C, Borisova A, Suomalainen M, Berghuis A, Halkosaari V, Kruus K, Pulkkinen L, Tirri T, Peura J, Kilpeläinen P, Saranpää	12/2018
Biannual progress report, months 19 - 24 (1.12.2018 - 31.5.2019)	Laine C, Borisova A, Suomalainen M, Heikkinen J, Kyllönen H, Pulkkinen L, Tirri T, Peura J, Kilpeläinen P, Saranpää	6/2019
Biannual progress report, months 25 - 30 (1.6.2019 - 30.11.2019)	Laine C, Rahikainen J, Suomalainen M, Behm K, Ohra.aho T, Pulkkinen L, Tirri T, Peura J, Kilpeläinen P, Saranpää P	1/2020
Deliverable reports		
D1.1 Literature and market study (month 3)	Alakurtti S, Kyllönen H, Laine C, Borisova A, Kuosa M, Saranpää P, Kilpeläinen P	30.11.2017
D1.2 Pilot production of crude tannin in 10 kg scale (month 3)	Alakurtti S, Salonen P, Willberg-Keyriläinen P, Laine C, Kruus K (VTT)	15.11.2017

Reports	Authors	Distributed
D2.1 Conditions for an optimal tannin extraction in batch process (month 14)	Kilpeläinen P, Saranpää P (Luke)	15.1.2019
D2.2 Procedure and processing parameters for tannin extraction in continuous process (month 24)	Kuosa M, Tirri T (Xamk)	31.5.2020
D2.3 Large batch of tannin produced with optimized extraction batch process (month 20)	Kilpeläinen P, Kaipanen K, Saranpää P (Luke)	14.5.2019
D2.4 Procedures for determining polyphenolics, stiasny-number and carbohydrates available for the partners (month 4)	Mikkelson A, Willberg-Keyriläinen P, Laine C, Alakurtti S (VTT), Saranpää P, Kilpeläinen P (Luke)	25.10.2017
D3.1 Purification of a larger batch of crude tannin to obtain enriched tannin fraction (month 28)	Borisova A, Heikkinen, J, Kyllönen H, Laine C (VTT)	28.10.2019
D3.2 Chemicals to improve tannin stability discovered and method for wet storage of tannin developed (month 28)	Rahikainen J, Laine C (VTT)	8.10.2019
D4.1 Tannin-wood-adhesives for particleboard, plywood and mdf (month 28)	BSc thesis, Tannin-based phenolic resins for plywood and laminates, Berghius A (VTT)	7.6.2018
D4.2 Tannin-hot-melt adhesives for packaging (month 28)	M.Sc. thesis, Tannins in sustainable hot melt adhesives, Halkosaari V (VTT)	19.12.2018
D5.1 Application and performance tests for tannin-wood-adhesives for particleboard, plywood and mdf (month 30)	Peura J, Tirri T (Xamk)	31.5.2020
D5.2 Applications and performance tests using formulated tannin-hot-melt adhesives for packaging (month 30)	Peura J, Tirri T (Xamk)	31.5.2020
D6.1 Light techno-economic analysis and design and techno-economics of the selected concept (month 36)	Suomalainen M, Hytönen E, Laine C, Alakurtti S (VTT)	14.5.2020
D7.1 A signed project agreement (month 1)	Signed by all partners	27.9.2017
D7.2 Detailed work plan (month 1)	Presented by research partners in the kick-off meeting	21.6.2017
D7.3. Research reports according to the instructions of Business Finland (month x, y, x)	Reports to Business Finland reports every 4th month	8 reports delivered
	Biannual reports to Consortium every 6th months (see above)	5 reports delivered
D7.4 Final report (month 36+2)		
D7.5 Basic information package of the project (month 1)	Basic information presented in kick-off meeting	21.6.2017

Reports	Authors	Distributed
D7.6 Dissemination plan (month 2)	Presented in Steering group meetings	
D7.7 Exploitation roadmap and plan (month 2 and month 36)		27.6.2018 update 31.5.2020

Task 7.2 Dissemination (VTT, Luke, Xamk)

The project results were disseminated mainly in conference presentations during the project. Several manuscripts for peer-reviewed publications are in progress.

Planned publications in scientific journals with peer review

- Kyllönen, H., Heikkinen, J. Borisova, A., Rahikainen, J., Laine, C., ' Enzymatic treatment and fractionation of pilot hot-water bark extracts from Norway spruce and Scots pine'
- Kilpeläinen et al. ' Modeling of pine and spruce bark extractions with seemingly unrelated regression'
- Kuosa et al. 'Review on continuous extraction'
- Kuosa et al. 'Continuous extraction of spruce bark tannin in a screw reactor'

Result webinar

Results were disseminated for participating companies and research institutions via an on-line result webinar organized 28.5. 10-12:30. Ca. 30-40 people viewed the presentations and participated in discussion.

Conference presentations

Kilpeläinen, P., Ilvesniemi, H., Saranpää, P, Venäläinen, M., Optimisation of tannin extraction from spruce and pine bark, Kokkola materials week 31.10.18, https://materialweek.fi/file/2018/Kokkola-Material-Week-2018-BioKokkola-Petri-Kilpelainen-Luonnonvarakeskus.pdf

Alakurtti, S., Tamminen, T., Kruus, K. Laine, C., Polyphenols from softwood bark in adhesive applications, 8th Nordic Wood Biorefinery Conference, October 22-25, 2018, Helsinki, Finland, Proceedings, VTT TECHNOLOGY 340, pp. 99-104.

Laine, C., Rahikainen, J., Borisova, A., Heikkinen, J., Kyllönen, H., Suomalainen, M., Anghelescu-Hakala, A., Halkosaari, V., Alakurtti, S., Kilpeläinen, P., Saranpää, P., Tirri, T., Kuosa, M., Softwood tannin biorefinery, oral presentation, 9th Nordic Wood Biorefinery Conference, NWBC 2020, Stockholm, October 2020.

Thesis works

Anneloes Berghuis / Bachelor thesis 4.2.2018 – 4.7.2018

- Hanze University of Applied Sciences, Groningen, The Netherlands
- Subject: WP4 / Tannin-based phenolic resins for plywood and laminates
- Thesis is public, thus two versions were prepared and finalised 21.6.2018
    - 1. Public

    - 2. Confidential with all details for project partners
- Veikko Halkosaari / Master thesis 2.5.2018 – 30.10.2018
    - Technical University of Tampere (TUT)
- Subject: WP4 / Tannins in sustainable hot melt adhesives
- Public thesis is available:
    - Halkosaari, V., Tannins in sustainable hot melt adhesives, M.Sc. thesis, Tampere University, published in January 2019. https://dspace.cc.tut.fi/dpub/handle/123456789/27040https://dspace.cc.tut.fi/dpub/handle/123456789/27040

IPR

One invention disclosure was filed at VTT during the project.

Public pages

There are alternatives to toxic phenol compounds used in glues!, The Making of tomorrow, VTT, https://makingoftomorrow.com/there-are-alternatives-to-toxic-phenol-compounds-used-in-glues/

Kuoresta arvokkaita yhdisteitä hartsi- ja liimasovelluksiin, Business Finland 'Case', 8.2.2019, https://www.businessfinland.fi/ajankohtaista/caset/2019/kuoresta-arvokkaita-yhdisteita-hartsi--ja-liimasovelluksiin/

Milestones and deliverables

- **MS 7.3** Project meetings organized (Month 6, 12, 18, 24, 30, 36)

- **D7.1** A signed project agreement (Month 1)
- **D7.2** Detailed work plan (Month 1)
- **D7.3.** Research reports according to the instructions of Business Finland (month X, Y, X)
- **D7.4** Final Report (Month 36+2)
- **D7.5** Basic information package of the project (Month 1)
- **D7.6** Dissemination plan (Month 2)
- **D7.7** Exploitation roadmap and plan (Month 2)

9. Conclusions

Hot water extraction of industrial softwood bark is a viable way of obtaining bio-based chemicals and thus more value from a major industrial biomass side stream.

If hot water extract (crude tannin) would be used to replace a bulk chemical such as phenol (market price 700-800 €/t), large scale production (7300 t/a) and large investments are necessary (30-40 M€). In addition, process integration to a pulp mill is essential. If higher value applications for hot water extract emerge (>1000 €/t), lower scale production may also become viable.

The SusBinders project evaluated the potential of hot water extracts (crude tannin) in adhesive applications. In phenol-formaldehyde resins max. 20% of phenol could be replaced (drop-in solution) with the softwood crude tannin without compromising performance of the adhesive. This level of replacement is modest and substantially more effort should be put in adhesive formulation to increase the proportion of crude tannin. In hot-melt adhesives crude tannin was found to improve processability and adhesion towards uncoated boxboard. The dark brown colour associated with tannin was found to be problematic in certain applications of hot-melt adhesives. On the other hand, crude tannin has a very pleasant forest-like scent which may be beneficial in some other applications.

Extraction yield is a critical parameter for process economics and the project targeted at improving the extraction yield by 50% by developing batch-mode and continuous mode extraction approaches. Radical improvements in extraction yield were not achieved and there is still room for improvements and novel ideas in this field.

The hot water extracts (crude tannin) are rich in carbohydrates (ca. 50% of total extract) and the project developed an approach for partial purification of tannin from carbohydrates by employing enzymes and memebrane filtration techniques. Enzymes were successfully used to degrade polymeric carbohydrates (ca. 50%) in the hot water extracts using commercially available enzyme preparates, but the separation of phenolic and liberated carbohydrate compounds using membrane filtration techniques turned out more challenging than anticipated. Separation of phenolic and carbohydrate compounds based on molecule size is not possible. Membrane filtration techniques were successfully used for concentrating the hot water extracts (crude tannin) which may be a more viable way of removing water from the end product.

Future work should focus on finding applications to crude tannin where properties of the extract are superior. These applications should ideally take advantage of the phenolic and carbohydrates present in the extracts. In addition, potential application fields may be found from foods, cosmetics, nutraceuticals and pharmaceuticals. However, these applications typically require further fractionation/purification of the crude extract and advanced analytical tools to detect the desired compounds.

10. References

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https://www.vttresearch.com/sites/default/files/pdf/tiedotteet/2000/T2045.pdf

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Kemppainen K. 2015. Production of sugars, ethanol and tannin from spruce bark and recovered fibres. VTT SCIENCE 76. ISBN 978-951-38-8215-0 (URL: http://www.vtt.fi/publications/index.jsp)

Laine, C., Willberg-Keyriläinen, P., Ropponen, J., Liitiä, L. 2019. Lignin and lignin-derivatives as components in bio-based hot melt adhesives, Journal of Applied Polymer Science 2019, https://doi.org/10.1002/APP.47983

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